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EVALUATION OF SEMIPERMEABLE MEMBRANES FOR CONCENTRATION OF ORGANIC CONTAMINANTS IN DRINKING WATER

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Gulf South Research Institute

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment -- air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

This report describes an investigation for a means of predicting the recovery of organic contaminants from drinking water by reverse osmosis. The work is an integral part of a project directed toward the identification and toxicological evaluation of these contaminants.

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Director
National Environmental
Research Center, Cincinnati

ABSTRACT

Membrane separation principles have been examined and tested for the separation of trace organic solutes from drinking water to facilitate toxicological sample preparation. Five membrane materials have been evaluated through experiment and through review of the literature. The membranes included cellulose acetate, cellulose acetate butyrate, ethyl cellulose, polyamide, and polyurea (NS-1). Two modes of operation were considered for the membrane. In one mode the driving force was applied by hydrostatic pressure, and in the other the driving force was created by an osmotically active "pump" solution. The former method corresponds to operation in the reverse osmosis mode; the second method has been termed osmotic ultrafiltration. An extensive literature review, screening the performance of the membranes toward separation of the vast majority of organics potentially present in drinking water, is given. Reflection coefficients σ were calculated for separation of several solutes by cellulose acetate and polyurea (NS-1) membranes; from these coefficients the preferred operating pressure for separation can be estimated. Experimental concentrations of selected solutes were carried out in an osmotic concentrator designed during this study. The concentrator operates at an effective pressure of up to 150 atm, depending on the concentration of the "pump" solute. With this device the response of separation and flux to driving pressure is easily measured. From separation experiments with cellulose acetate membrane, two classes of organic compounds (classified according to their response in the separation system) were identified. One class of compound shows increasing separation with increasing applied pressure; the other class shows anomalous response of separation to increasing pressure, with some solutes maintaining constant rejection, and others showing decreased rejection with increased pressure. The results were in accord with reverse osmosis observations reported in the literature.

To study the separation mechanism, permeability coefficients $\overline{p}$ and distribution coefficients S (of solutes between membrane and water) were measured. These parameters were correlated with the actual separation achieved with the membranes. The solution diffusion mode was used to explain the transport phenomena through the membrane. The main conclusion derived from this approach was that high water-solute coupling occurs in transport. Polyamide and polyurea (NS-1) were shown to yield high separation and low permeability compared to the cellulosic type membrane.

High rates of water removal were demonstrated in the laboratory osmotic ultrafiltration unit. Concentration of large volumes of water by a factor of 10X using reverse osmosis, followed by a further concentration of 50X with the osmotic concentrator is shown to be a reasonable approach to

sampling large volumes of drinking water for toxicological analysis of the residues.

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CONCLUSIONS

1. The results of this study, combined with data from the literature, indicate the feasibility of concentration and recovery of organic solutes from water samples by osmotic techniques (i.e., reverse osmosis and osmotic concentration).

2. The degree of recovery of organic solutes varies with the particular solute-membrane combination.

3. The rejection of salts by a membrane is a good indicator of its mechanical integrity, but is not a good indicator of its potential utility in concentration of organics.

4. Solute recovery is influenced by the applied pressure (osmotic or hydraulic). This response to pressure may be crucial, especially in the concentration of low molecular weight compounds. Preknowledge of the σ value for a particular solute-membrane combination is useful for estimation of the pressure to be employed.

5. Two possible mechanisms are involved in the retention of solutes by a membrane. The first mechanism is utilized by the NS-1 membrane, where a highly cross-linked surface structure of the membrane mechanically limits molecular penetration by the solute. The second mechanism is utilized by the cellulose acetate membrane, where chemical interaction is the dominant factor of the retention behavior.

6. The cellulose acetate-derived membranes show the least overall rejection toward organics, but are chlorine resistant and exhibit excellent salts rejection and water permeability. They thus serve as satisfactory first-separation membranes.

7. The polyurea and polyamide membranes show very good rejection characteristics toward a wide variety of solutes, and are best suited for final concentration; i.e., to process the permeants from cellulose acetate membranes. These permeants are chlorine free, but may contain certain organics.

8. The theoretical concepts for the rejection of organics by semipermeable membranes require further study. Simple models relating affinities between pure solutes and pure polymers are not sufficient to provide quantitative estimates of rejection. However, this report examines models based on competitive interactions of the triple component system, water-solute-membrane. These models may provide the basis for such predictions of rejection.

CONCLUSIONS CONCERNING REVERSE OSMOSIS (RO) AND OSMOTIC CONCENTRATION (OC)

9. For short concentration runs of several hours, the rejection expected from the OC runs is higher than expected from RO. The opposite applies for long term runs.

10. Large volumes of water should be more easily handled with RO processes. Small volumes are better handled by the OC process.

11. RO is limited to relatively low hydraulic pressure application. Membrane compaction, mechanical damage, and high costs of instrumentation are some of the problems concerned with high pressure application in reverse osmosis. Very high osmotic pressure can be applied in the OC procedure without any changes in the membrane properties and with simple, low-cost instrumentation.

RECOMMENDATIONS

1. The results of this study indicate that concentration of organic solutes by reverse osmosis or by osmotic ultrafiltration is a feasible process. The practical application of these techniques to large volume samples is required to identify and solve problems associated with scale-up of equipment. It is a recommendation of this program that controlled concentration experiments of 500-1,000 gallons be performed, to establish firmly the recovery efficiencies that may be expected.

2. The processing of large volumes of water containing trace levels of organics requires equipment which will not contribute artifacts to the resulting sample. Studies must be performed to establish the material and procedural requirements for reliable concentrated samples.

3. Application of the results reported in this study require the development of test protocols for concentration, and for the processing of concentrates for analysis and feeding studies. Such protocols can best be developed by using seeded samples of purified water having known solute concentrations. A program to establish these protocols is suggested, so that savings in field study costs can be achieved.

4. Current understanding of the rejection of organics is still highly empirical. Further work must be scheduled to extend our ability to project the response of membrane rejection to solute species, pressure, temperature, and pH. Such ongoing studies are required to build an adequate data base for future use of the method in a variety of waste water systems.

5. The development of a highly cross-linked, charged asymmetric membrane is recommended by this study. Rapid progress in membrane technology has made this a possible goal to achieve in the near future.

6. For the reverse osmosis concentration process, simultaneous operation of two steps in sequence, employing two different types of membrane, is recommended. The membrane to be employed in the first step is a cellulose acetate membrane which exhibits very high salt rejection, high water permeability and chlorine resistance. Organic compounds of high molecular weight will be retained by the membrane and will be collected in this step. However, several organic compounds of low molecular weight will permeate through the membrane as a result of the overall low rejection property of the membrane; others, e.g., phenols, will permeate as a result of operation at a low pH of 5.5-6. These compounds of low molecular weight will be concentrated in the second step, where polyamide or polyurea (NS-1) membranes will be employed. Relatively high pH could be used in the second step. Thus excellent rejection of phenol and organic acid could be achieved. The low ionic strength of the solution (the result of high salt rejection of cellulose acetate) is an important factor leading to enhanced concentration efficiency of the low molecular weight compounds in the second range.

7. The overall scheme of concentration proposed by this study is as follows:

   Large volumes of water are to be concentrated in an RO device. When the osmotic power of the concentrated solution becomes high (as a result of salt buildup) a substantial decrease in flux through the membrane may be observed. Further concentration should employ an OC procedure. Since the ionic strength in the concentrated solution is relatively high, a charged membrane (high dielectric media) is recommended for the OC device in this step. At present the protonated NS-1 membrane can be used as a charged membrane while maintaining the solution at pH less than 10.8.

1.0 INTRODUCTION

The toxicity of organic chemicals found in drinking water supplies has become a matter of increasing concern (1-2). Definition of real or potential hazards in drinking water supplies requires information on the kind and concentration of solutes present. Because of the very low concentrations (less than 5 ppm) of such solutes, analytical and toxicological procedures dictate that some method of concentration must precede such definition. The concentration procedure must be capable of dealing with large sample volumes, and should leave the composition and the relative concentrations of the solutes unchanged. As with the case of isolating fragile viral particles, the investigator has the choice of retaining the particle (or solute) of interest on a suitable substrate from which it can be eluted, or of removing large quantities of water from the test solution (3).

Practically, the recovery of trace quantities of organic chemicals from potable water supplies poses severe technological problems to the concentration process used. It is necessary to arrive at a scheme which will concentrate the solutes in a suspect water sample without causing chemical alterations that will work against analyses. This must be done within a time frame that permits real-time control steps. Furthermore, the scheme ideally should be able to cope with the almost infinite variety of organic chemicals that may be present in miniscule amounts in water supplies.

Middleton et al. (4) have investigated the use of activated carbon for the adsorption of trace organics followed by elution by chloroform and/or alcohols. This method does not lead to quantitative recovery. Also, chemical modifications can occur, and for some species, especially high molecular weight compounds, the elution is negligible. The adsorption of organic compounds from water by use of cross-linked polymers has been described recently (5). The adsorbent resin used was porous polystyrene cross-linked into a matrix with divinylbenzene (40-60 mesh). Good adsorption of the organics, which have poor water solubility, has been achieved by this process. Re-extraction of the organics from the adsorbent resin gave good recovery of hydrophobic organics. While the recovery is improved, this method does not yet offer broad spectrum recovery of organics. Neither of these methods recover adequate quantities of materials for toxicity studies.

In an earlier publication from this laboratory (3), a process to concentrate viral particles in drinking water was reported. The process employed an osmotic pressure generated across a semipermeable membrane as the driving force to remove quantities of water. The viral particles, consisting of large protein and DNA segments, were retained, and the concentration required for subsequent quantitation was achieved by tissue culture methods. The present paper is an analysis of a related problem: the concentration and retention of trace organic chemicals from potable water. In the present study attempts were made to devise an analytically sound concentration method based on membrane separation techniques. There are two major aspects of this study. The first is evaluation of currently available membranes for the task of concentrating trace organics in water. The second is derivation of a consistent framework for predicting the ability of any membrane to concentrate a wide spectrum of organics found in water. This second task requires a basic understanding of the permeabilities and diffusivity mechanisms of the organics and water within selected membranes.

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1.1 PRINCIPLES OF OSMOSIS, REVERSE OSMOSIS, AND OSMOTIC ULTRAFILTRATION

1.1.1 Osmotic Pressure Relationships

The theoretical basis for separating solutes from aqueous solutions by use of semipermeable membranes is illustrated in Figure 1. Consider two solution compartments of volumes V_1 and V_2 separated by a membrane M. Compartment V_1 is filled with an aqueous solution containing a trace level of organic solute, and compartment V_2 is filled with an aqueous solution containing a significant concentration of osmotic solute (e.g. concentrated solution of an inorganic salt), which is termed the pump solution. Each compartment experiences an applied hydrostatic pressure given by P_1 and P_2. We now ascribe to the membrane semipermeability (i.e., it is impermeable to all solutes, but permeable to water). As a result of the solute concentrations in the compartments,osmotic pressures π_1 and π_2 are generated. Water transport through the membrane can now be predicted for selected inequalities of the gradients described above:

1. If $P_1 = P_2$, and $\pi_2 > \pi_1$, then water will flow from V_1 into V_2, and the solutes in V_1 will be concentrated. This is a simple osmotic concentration (OC) process.
2. If $(P_2 - P_1) = (\pi_2 - \pi_1)$, no water flux will occur. This will always be the final state of an isolated system.
3. If $(P_2 - P_1)$ is greater than $(\pi_2 - \pi_1)$, water will flow from V_2 into V_1; this process, the reverse of case 1 above, is termed reverse osmosis (RO).

The first case described above, osmotic concentration (OC), has also been termed "osmotic ultrafiltration" (OU) in an earlier publication (3) because ultrafiltration of the solute is effected by osmotic driving force. In the present study OC will be the term for concentration by osmosis and OU will refer to the transport through a membrane by osmosis.

The water flux described above as case 3 is generated by hydraulic pressure. The concentration of organics by the reverse osmosis method can be schemed as follows: Compartment V_2 (Figure 1) is filled with the water solution that is to be concentrated. Pure water is placed in V_1. Even if no salts are present in V_2, the balanced osmotic pressure in the cell will be $\pi_2 > \pi_1$. To achieve concentration of the organics it is necessary to maintain the condition $(P_2 - P_1) > (\pi_2 - \pi_1)$.

For the solutes to become concentrated, the membrane selected must not be permeable to the species followed. The degree of nonpermeability in the presence of a flux of water through the membrane is termed the rejection of the solute by the membrane. The degree of rejection is a direct function of the membrane type, the solute species, and the rate of water flux through the membrane.

The osmotic transport which is described in case 1 above is an ideal situation since it considers the membrane as a perfect barrier to the solutes in both compartments. Unfortunately this is not the case in practical operations, as membranes with this degree of perfection have not been prepared. Thus it is very important to be able to describe the degree of "imperfection" or the so-called rejection value of the membrane toward every solute which might be encountered in this concentration procedure.

The rate of water transport through the membrane is a significant variable in determining the efficiency of this process. Substantial quantities of water must be transported through the membrane so that the residue of solution is concentrated sufficiently for toxicological analyses. The rate of water transport per unit area of membrane is termed hydraulic permeability. A material coefficient called the hydraulic permeability constant (L_p) exists for each membrane; its value will be defined in this section.

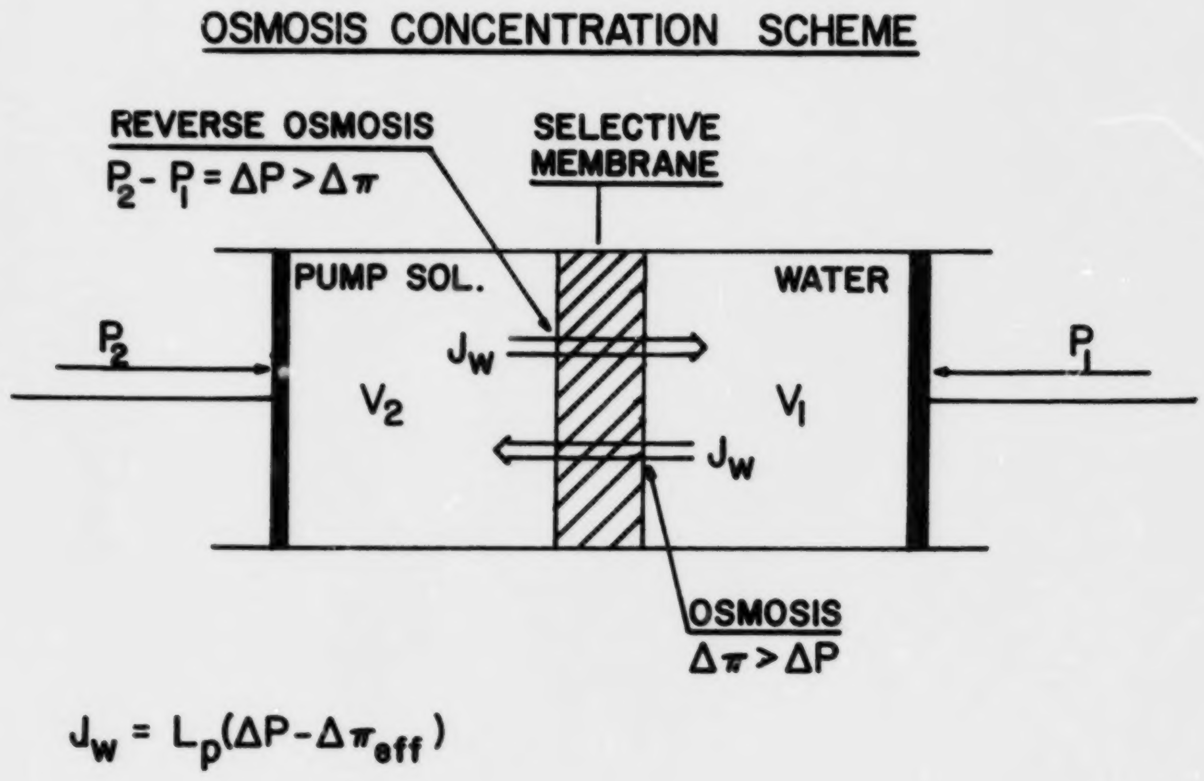
OSMOSIS CONCENTRATION SCHEME
REVERSE OSMOSIS
$P_2 - P_1 = \Delta P > \Delta\pi$
SELECTIVE MEMBRANE
PUMP SOL.
WATER
P_2
P_1
J_w
V_2
V_1
J_w
OSMOSIS
$\Delta\pi > \Delta P$
$J_w = L_p(\Delta P - \Delta\pi_{eff})$

Figure 1: Osmosis concentration scheme.

Similarly, the rate of solute transport through the membrane will affect the recovery of solutes during the concentration process. The solute permeability also is a function of the membrane material, the properties of which often vary with the concentration of solute in the membrane. However, because this study deals with trace levels of solutes, changes in solute concentration in the membrane are not significant here.

Three main parameters are to be considered in every membrane concentration process: (1) water flux through the membrane, (2) the solute flux through the membranes, and (3) the rejection of the solute by the membrane.

1.1.2 Water Flux and Hydraulic Permeability

According to the considerations stated above, the water flux through the membrane is directly proportional to the net pressure applied; it thus can be described by the equation:

$$J_w = L_p \left[(P_1 + \pi_2) - (P_2 + \pi_1) \right] \qquad (1)$$

where J_w = the flux of the water per unit area (expressed in terms of $ml \cdot sec^{-1} cm^{-2}$)

P = hydraulic pressure (atm)

π = osmotic pressure generated by the solutions (atm)

L_p = the hydraulic permeability constant, which must be evaluated for each membrane ($ml \cdot sec^{-1} cm^{-2} atm^{-1}$)

Since the net driving force for the water flux can be either the hydraulic pressure (RO) or osmotic pressure (OC), equation (1) is valid for both cases. Thus the total expression in parenthesis in the equation can be designated ΔP (i.e., the resultant pressure), and equation (1) can be reduced to

$$J_w = L_p \Delta P \qquad (2)$$

From this equation one can see that L_p is equal to the flux of water through the membrane (J_w) when the net pressure difference is 1 atm. L_p is one of the most important practical constants for the concentration process, especially as it affects the choice of membrane. For example, with knowledge of the L_p of a membrane one can adjust the pressure (osmotic or hydraulic) to the time limit of the concentration runs.

1.1.3 Solute Flux Equation

The diffusion theory developed by Fick (6) provides an independent equation for each solute flux through the membrane:

$$J_s = \overline{P}\ (C_f - C_p) \qquad (3)$$

where J_s = solute flux (g $cm^{-2}sec^{-1}$)
$\overline{P}$ = permeability coefficient of solute (cm sec^{-1})
C_f = solute concentration in the feed mixture (g cm^{-3}), i.e., the mixture that is to be concentrated
C_p = solute concentration in product solution (g cm^{-3})

Equation (3) indicates that the driving force of the solute through the membrane is the difference in the concentration of the solute on either side of the membrane, i.e., $C_f - C_p$. For osmotic concentration (OC), C_p in equation (3) will be the concentration of solute in the "pump solution" of Figure 1. (Since the pump solution has an ionic strength different from that of the feed solution, the activities of the solute instead of concentration must be taken for practical calculation.) For reverse osmosis (RO), C_p will be the direct concentration of the solute in the liquid phase permeating out from the membrane, i.e., $C_p = J_s/J_w$. Equation (3) does not consider the pressure influence on the solute flux, which is influenced by pressure in RO. However, the influence of hydraulic pressure on solute permeability is negligible for the present case, since this study deals with trace concentrations of solute, and a very large pressure change is required to change the activity or the chemical potential of the solute by an amount equal to the change produced by only a small concentration change. From equations (1), (2), and (3) one can see that the driving forces of J_s and J_w are different. The diffusion mechanism in solutions as derived by Lonsdale et al.(7-8) treats the transport phenomena as if water and solute were two independent flows. That is, J_s is the independent flux of solute and is not coupled with the water flux. It will be shown from the results of this study that the fluxes of many organic compounds are coupled with that of water and that adjustment of equation (3) must be considered.

The permeability coefficient $\overline{p}$ in equation (3) is a parameter which is dependent on the properties and interactions of the specific solute-membrane combinations. Especially in the transport of organic solutes, $\overline{p}$ is a very "sensitive" coefficient. Changes in pH, ion strength of solution, and in other variables may have a crucial effect on $\overline{p}$, especially during the concentration process. Thus such changes affect the efficiency of the overall concentration in both RO and OC systems. A full discussion of the permeability coefficient $\overline{p}$ is included in Part II.

1.2 SOLUTE REJECTION

The rejection, R, of a specific solute is defined by the relationship:

$$R = 1 - C_p/C_f \tag{4}$$

where, in the cases of both OC (for osmotic pressure) and RO (for hydraulic pressure), C_p refers to that solute's concentration in the transported water ($C_p = J_s/J_w$). From equations (1) - (4) it is possible to derive equation (5).

$$R = \frac{L_p \Delta P}{L_p \Delta P + \overline{p}} \tag{5}$$

For derivation of equation (5) see Part II, Chapter 4.

Equation (4) gives the direct definition of rejection; two simple parameters (C_p, C_f) are measured experimentally to determine R. Equation (5), however, requires only one parameter ($\overline{p}$) to obtain the rejection that is to be anticipated from a specified membrane-solute concentration system. That is, if one knows $\overline{p}$, the permeability coefficient of a solute in a membrane, he can calculate the rejections over a wide range of arbitrary values for ΔP. Equation (5) indicates that as water flux increases, R approaches its maximum value. In the ideal case where $L_p \Delta P \gg \overline{p}$, R approaches 1.0. Equation (5) has the merit of predicting the rejection without the requirement of direct experimental determination of a pressurized system. Comparisons of the experimentally measured R of equation (4) and R calculated from equation (5) would give information on the solute transport mechanism in the membrane, and would indicate whether the solute transport is coupled with the water flux. This comparison is meaningful because the formulation of equation (5) does not consider coupled fluxes, since it is derived from equation (3). Here is a most important point to practical concentration operation. If equation (5) is valid for a system, and uncoupled fluxes occur, then operation with high ΔP is advocated. If equation (5) is not valid, increased pressure may reduce R; such cases are discussed later in this part of the report. Other considerations, to be discussed below, also must be taken into account.

Two more considerations pertain to equations (4) and (5):

1. Equation (5) was developed directly from the mechanism involved in reverse osmosis (RO) systems. For osmotic concentration (OC) systems the highly concentrated media of the pump solution may help to provide better rejections than are anticipated from equation (5). (For considerations of the high chemical potential or organic solutes in a strong ionic medium, see Part II.)
2. Equations (4) and (5) indicate that R is independent of the membrane thickness.

1.3 MEMBRANE SELECTION CRITERIA

On the basis of the objectives defined above, the following criteria for the selection of membranes to achieve concentration have been formulated.

1. The membrane should be either commercially available or in an advanced developmental stage.
2. The membrane should have a large hydraulic permeability coefficient L_p so that practically attractive rates of concentration can be attained in relatively short time.
3. The membrane should be suitable for use either in reverse osmosis or in osmotic ultrafiltration equipment.
4. The membrane should be of a material expected to show good rejection for a large number of organic solutes.

After membranes meeting these criteria have been selected, it is necessary to devise experimental protocols to characterize the membranes with respect to their $\overline{p}$ and L_p values. With these data one can expect to predict the behavior of membranes for use both as reverse osmosis barriers and in an osmotic ultrafiltration device.

Some background will help clarify discussion of these criteria. The membrane technology which is based on diffusion processes (as opposed to simple filtration and dialysis) is a young technology. Its major impetus came in the early 1960s, when Loeb and Sourirajan (9) developed the asymmetric cellulose acetate membrane. Since the 1960s the major efforts of membrane development were directed toward water desalination, especially of brackish and sea water. Membranes were designed to meet the requirements of high hydraulic permeabilities and high salt rejections. The rejection of organic trace contaminants has had only minor importance in the development of such membranes. These membranes are the only ones that match the first three criteria given above. The present study demonstrates the potential of known semipermeable membranes for concentration of trace organics. However, the data reported here indicate that to simplify the process for practical one-step concentrations, it will be desirable to develop a new membrane capable of achieving rejection for a broad spectrum of organic solutes. Some suggestions are given in the conclusions of this study.

1.3.1 Productivity

The flux of water through the membrane is inversely proportional to the membrane thickness. In equation (1), J_w does not account for membrane thickness because this equation was developed for a given membrane regardless of its thickness. To achieve high water flow through known polymers, the effective thickness of the membrane must range between 10^{-4} to 10^{-5} microns. High (or sufficient) water flow means L_p values in the range of 10^{-6} to 10^{-5} g $cm^{-2}sec^{-1}atm^{-1}$*. Since no known polymeric material of the given thickness is strong enough to withstand even low hydraulic pressure, an asymmetric membrane has been developed (9). This type of membrane consists of two layers: a dense, active layer which resembles the membrane properties, and a spongy porous support layer which gives the membrane its mechanical strength properties (see Figure 31). The support layer itself should have the ability to withstand high hydraulic pressure (that is, to resist compaction) under RO conditions. No compaction of the support layer occurs under $\overline{OC}$, where only high osmotic pressures are employed. This gives the OC system a general advantage over RO by allowing selection of a larger variety of asymmetric membranes. See Appendix A for more details on asymmetric membranes. For advanced literature see reference (10).

1.3.2 Solute Sorption Losses

The membranes used in the concentration operation all are made of organic polymers which have the ability to absorb organic compounds. Some solutes are strongly sorbed; others are not sorbed at all. Thus, the organic solute in the water may be distributed between the water phase and the membrane (polymeric) phase. Equation (6) defines the distribution coefficient S of a system in which a membrane is immersed in water solution until the solute reaches a state of equilibrium:

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*From equation (1) it is possible to calculate the order of magnitude of J_w related to this L_p range.

$$S = \frac{\dfrac{\text{Wt solute in membrane}}{\text{Wt (membrane + solute)}}}{\dfrac{\text{Wt solute in water}}{\text{Wt (solute + water)}}} = \frac{C_{sm}}{C_{sw}} \qquad (6)$$

where Wt = weight

C = concentration s = solute m = membrane

The distribution coefficient is a constant dependent on the membrane material, the organic solute, and the temperature. Changes in the water phase (e.g., the addition of salt ions), or changes in the membrane phase (e.g., plasticization), may cause significant changes in S. The fact that organic solutes can be substantially absorbed by the membrane raises three important points concerning RO or OC procedures:

1. Membrane absorption--even when rejection is high--must be considered when processing decisions are made. While increased membrane area provides more rapid processing rates, the loss of trace solutes to the membrane should be estimated when distribution coefficients, S, are known.
2. Since the main objective of the concentration processes is to collect the organic solutes, the concept of rejection defined by equation (4) must, from a practical point of view, consider not only C_p but also the loss of solute to the membrane. (In desalination studies C_p usually is measured directly from the solute concentration in the permeating water.) The loss of solute through permeation and sorption can be determined experimentally by calculating and extrapolating C_p from the net decrease of solute in feed solution.

3. Equation (18) in Part II will show that the permeability of solute through the membrane is directly proportional to S. One might conclude that as a consequence of high S values low rejection is to be found. This is the case in many membrane processes. However, nowhere in the literature could hard evidence be found to support this conclusion for the systems described in this report. The relationship between S values and rejection was investigated as part of this study and is reported.

1.4 PROGRAM OBJECTIVE

The objective of this project has been to evaluate the potential for concentrating and recovering trace organics in water supplies by means of osmotically driven concentration processes. To establish the efficacy and operating parameters of such processes the following program steps were undertaken:

1. Identification and testing of membranes having high ultrafiltration coefficients; the test program included a comparison of organic rejection under both reverse osmosis and osmotic concentration conditions.
2. Selection of a broad spectrum of organic compounds representing a cross-section of functionalities and physical properties.
3. Comparison of the potential recovery of organics when concentrated by both RO and OC procedures.
4. Measurement of physical constants for selected membrane/solute combinations; these include determination of hydraulic permeability (L_p), permeability coefficient ($\bar{p}$), rejection (R), and distribution coefficient(S) as defined earlier.
5. Comparisons of experimentally measured rejections (R) with values calculated by either equation (4) or equation (5).
6. Identification of operating parameters identified as significant in field applications.

In addition to the programmatic items listed above, some study was required to identify the governing mechanism of solute permeation under the conditions of the test program. These results and their relationships to current transport theory are elaborated in Part II.

2.0 EXPERIMENTAL

This section describes the methods used to evaluate the parameters mentioned in section 1. A complete description of an apparatus for osmotic concentration (OC) is given. The reverse osmosis (RO) data are taken from the literature; description of an RO concentration scheme also is included in this chapter.

2.1 MATERIALS

2.1.1 Membranes

The first three criteria in section 1.3 led to the selection of the following three membranes for study:

Cellulose Acetate-- This membrane was prepared from a blend of cellulose diacetate and cellulose triacetate, to yield an overall degree of substitution of 2.75. The membrane was asymmetric, with a gross thickness of 93-100 microns.

Ethyl Cellulose-- This membrane was fabricated by a technique developed previously at GSRI (11). Membranes were prepared in three thicknesses: 15-20, 25-35, and 45-55 microns. The polymer was a cellulose ether containing 2.25% ethoxy groups.

NS-1 Composite Membrane-- This membrane was developed by North Star Research Institute (12). It is an ultrathin film formed by the reaction of a polyamine and a diisocyanate, supported by a porous membrane prepared from polysulfone. The thin layer is not chemically bonded to the substrate, but is maintained there by surface forces.

The cellulose derivative membranes were prepared by water-quenching a polymer film cast in an organic solvent. The membranes must be kept wet with water in order to prevent irreversible changes in their permeation properties. The NS-1 membrane was prepared dry and could be stored that way.

Note: the cellulose acetate membrane is commercially available for large concentration runs and is now used by GSRI for field trials.

The NS-1 membrane is currently under development for future commercial production. The ethyl cellulose membrane is not yet available commercially but can be ordered in small quantities.

During the course of this study only one additional membrane became commercially available: a nylon hollow fiber membrane. This membrane is now under study for concentration purposes at GSRI. A review of recent literature reporting the performance of RO experiments with cellulose acetate butyrate and polyamide membranes is included in the discussion.

2.1.2 Solutes

The solutes used for testing permeation were of analytical grade. The specific solutes were selected to provide a representation of specific properties. Solutes were selected to include:

1. One representative compound from each of 20 organic functional classes;
2. Compounds previously found by other researchers in drinking water supplies;
3. Compounds of known or suspected toxicological importance;
4. Compounds of known solubility parameters so that results can be meaningfully interpreted in view of solubility theories;
5. Compounds amenable to the analysis technique chosen;
6. Compounds of minimal molecular weight and bulk so that the extreme cases are tested.
7. Compounds of low vapor pressure because high vapor pressures will render analyses more difficult; furthermore, volatile compounds can be handled by other techniques;
8. Compounds that do not react with the membrane.

The compounds currently in the chosen list are presented in the following tables. Some compounds are compromises of the above factors and, therefore, do not fit perfectly under their given classes while others fit under several classes.

2.2 PERMEABILITY MEASUREMENTS

The permeability coefficient $\bar{p}$ was determined by use of the rotating diffusion cell described previously (13). The cell has two solvent compartments divided by the membrane to be evaluated. A solution of the solute to be tested is placed on one side and an equal volume of solvent is placed on the other side. The cell is rotated for a specified period at a given angular velocity to reduce concentration polarization. Both sides are then analyzed for solute concentration. Mass balances, permeability coefficients, and absorption are then calculated from these data.

Water solutions for the permeability measurement were mixed at the lowest practical concentration compatible with the analysis method used. This required some trial and error for each solute, but generally concentrations of 0.03-0.10 g/liter are sufficient for analysis by ultraviolet (UV) or total carbon (TC) techniques. Unfortunately, some of the compounds we desired to evaluate did not have sufficient water solubility for analysis methods used to date. These included phenylmercuric chloride, diethylstilbesterol, and D.D.T. The solubility of naphthalene falls at the lower limit acceptable for UV analysis.

Acidic and basic compounds were prepared in solutions containing tris-(hydroxymethyl) aminomethane (tris) buffer, pH 7.5. The tris buffer exhibits no absorption in the UV region, but use of tris obviates usage of the TC method. Selected compounds and methods of analysis are given in Table 1.

In certain cases where large amounts of compounds were absorbed on the cell wall or on the membrane surface, a "double load" technique was used. In this procedure the cell with the membrane is equilibrated with a solution of known concentration, additional solution of a higher concentration is added to one side, and transport of the additional material is then monitored.

TABLE 1 SELECTED COMPOUNDS AND METHOD OF ANALYSIS

Class	Compound	Method
1. Aromatic	Benzene	U.V., R
	Naphthalene	U.V.
2. Substituted Aromatic	o-Xylene	U.V.
	Dimethyl phthalate	U.V.
	*Benzene Sulfonic Acid	U.V.
	*Benzoic Acid	U.V.
	*Phenol	U.V.
	*Chlorophenol	U.V.
	Diethyl stilbestrol	U.V.
3. Heterocycle	*Pyridine	U.V.
	Diquat	U.V.
	Simazine	U.V.
4. Cycloalkane	Cyclooctadiene	U.V., T.C.
5. Alcohol	Allyl Alcohol	U.V.
	Cholesterol	R.
	Pentanol	R
6. Aldehyde	Furaldehyde	U.V., R
7. Ketone	3-Pentanone	U.V.
8. Di-acid	*NTA	G.C.
	*Malonic acid	R
9. Carboxylic	*Benzoic acid	U.V.
	*Heptanoic	R
10. Amines	*Aniline	U.V.
	*Allyl amine	U.V.
11. Hydrocarbon	Heptadecane	R
12. Chlorinated Hydrocarbon	D.D.T.	R
	Chlorobutane	G.C.
	Tetrachlorodibenzo-p-dioxane	U.V.

	Class	Compound	Method
13.	Salts	Na Benzoate	U.V.
		Na_3NTA	U.V.
		Na Butyrate	TC
14.	Ester	Dimethyl phthalate	U.V.
		i-Butyl acetate	U.V.
15.	Ether	bis-Chloroethyl ether	TC., GC.
16.	Amide	*Acrylamide	U.V.
		*Dimethylhydantoin	U.V.
17.	Nitroso	N-Nitrosodiethyl amine	TC
18.	Misc.	Glutaraldehyde	U.V.
		Methylmethacrylate	U.V.

* Buffered to pH 7.5 with tris-(hydroxymethyl) amino methane.

U.V. = ultraviolet spectrophotometry;

R = radionuclide tagged solute;

TC = total carbon analyzer.

The solute concentrations were determined by UV analyses on a Varian 635 spectrophotometer. Carbon analysis was performed on a Beckman Process Carbonaceous Analyzer. Working curves of standard solutions were determined for both methods. Blanks were run to determine solvent purity and also to determine that cells are completely free of interfering substances.

The permeability coefficient $\bar{p}$ was determined from the rotating cell data by equation (7):

$$\bar{p} = \frac{1}{tA\left(\frac{1}{V_t^a} + \frac{1}{V_t^b}\right)} \ln \frac{C_o^a - C_o^b}{C_t^a - C_t^b} \qquad (7)$$

where t = time (sec)

A = surface area of exposed membrane (cm^2)

V_t^a = volume of solution on side A of cell at time t (cm^3)

V_t^b = volume of solution on side B of cell at time t (cm^3)

C_o^a = initial concentration of solute, side A

C_o^b = initial concentration of solute, side B

C_t^a = final concentration of solute, side A

C_t^b = final concentration of solute, side B

V_t^a and V_t^b were essentially equal for all solutions. The value of c_o^b was always 0. The value of $\bar{p}$ varied from 0.01×10^{-5} cm/sec for benzene sulfonic acid to 32.5×10^{-5} cm/sec for cyclooctadiene. Equation (7) neglects the absorption of solute in the membrane. This is acceptable if the total loss of solute to the membrane is relatively small. (For further discussion of this equation and methods for evaluation of $\bar{p}$, see ref. 7.) The absorption by the membrane and cell was calculated from the ratio of the difference of the starting concentration minus the concentrations at time t to starting concentration:

$$\text{Absorption } \% = \frac{C_o^a - (C_t^a + C_t^b)}{C_o^a} \times 100 \qquad (8)$$

(see Table 2)

Because of absorption of some solutes, C_o^a of equation (7) was obtained in the practical calculation of $\bar{p}$ according to $C_o^{a1} = C_t^a + C_t^b$. As calculated in this experiment, $\bar{p}$ is a first order approximation which is suitable for this study.

Partial dissolution by resorcinol of both the cellulose acetate and ethyl membranes is evidenced by the apparent gain in total concentrations of side A and side B. Similar, but much more pronounced, evidence was observed for allyl amine and dimethylhydantoin, indicating extensive membrane degradation.

A sample calculation of permeability coefficient $\bar{p}$ is given for the solute benzoic acid buffer with a cellulose acetate membrane. Values for parameters of equation (7) are given below.

SAMPLE CALCULATION OF PERMEABILITY COEFFICIENT $\bar{p}$

Run	Solute	Membrane
97	Benzoic Acid/Buffer pH 7.5	Cellulose Acetate

λ = 225.4 μm.

$V_o^a = V_o^b = V_t^a = V_t^b$ = volume on each side of membrane = 25 ml

C_o^a = initial concentration, side a = 0.5930 g/l

C_o^b = initial concentration, side b = 0.0 g/l

C_t^a = final concentration, side a = 0.5575 g/l (from standard working curve)

C_t^b = final concentration, side b = 0.0045 g/l (from standard working curve)

TABLE 2 ABSORPTION OF ORGANIC COMPOUNDS IN PERMEABILITY MEASUREMENTS

Compound	Cellulose Acetate Abs (%)	Ethyl Cellulose Abs (%)	NS-1 Abs (%)
Benzene	1.48	33.64	4.65
O-Xylene	83.25	100	6.45
Benzene sulfonic acid*	22.74	9.72	40.0
Benzoic Acid	5.23	6.83	8.98
Phenol*	15.58	17.92	12.99
Chlorophenol*	34.32	38.18	30.56
Naphthalene	94.86	100	-
Allyl Alcohol	Membrane Interaction	Membrane Interaction	∿1
Furaldehyde	11.61	7.54	13.33
Ethyl Methyl Ketone	-15.68	-6.83	
Aniline*	11.80	7.27	3.5
Allylamine*	Membrane Interaction	Membrane Interaction	Membrane Interaction
Dimethylphthlate	19.7	26.85	9.80
Cyclooctadiene	13.08	100	9.26
Pyridine*	1.15	3.44	3.85
Acrylamide*	-9.51	Membrane Interaction	2.13
Dimethyl Hydantoin	Membrane Interaction	Membrane Interaction	Membrane Interaction
Glutaraldehyde	20.42	6.97	12.44
Methylmethacrylate	17.02	10.25	6.56
Sodium Benzoate	28.02		
Trisodium NTA	59.97	17.66	
Sodium Butyrate	17.26		

* Buffered to pH 7.5 with tris(hydroxymethyl aminomethane.

All analyses performed by ultraviolet except furaldehyde and methylmethacrylate for ethyl cellulose which were analyzed by total carbon.

$t = 30.0$ min.

$C_o^{a^1} = C_t^a + C_t^b =$ effective initial concentration, side a = 0.5620 g/l

$C_o^a - C_o^{a^1} =$ concentration lost to absorption = 0.0310 g/l

$C_t^a - C_t^b =$ difference of final concentrations = 0.5530 g/l

$$\bar{p} = \frac{1}{tA\left(\frac{1}{V_t^a} + \frac{1}{V_t^b}\right)} \ln \left(\frac{\Delta C_o}{\Delta C_t}\right) \qquad (7)$$

$$= (9.418 \times 10^{-5}) \ln \left(\frac{0.5620}{0.5530}\right)$$

$$= 1.5 \times 10^{-6} \text{ cm/sec}$$

$$L_p = 1.0 \times 10^{-5} \text{ g/cm}^2 \text{ sec}$$

(For L_p's see Table 5.)

Projected Rejection:

$$R = \frac{L_p \Delta_P}{L_p \Delta P + \bar{p}} \qquad (5)$$

Assume $\Delta P = 54.4$ atm (800 psi)

$$\text{Then} \quad R = \frac{(10^{-5})\ (54.4)}{(10^{-5})\ (54.4) + 0.15 \times 10^{-5}} => 0.99$$

The experimental procedure for the "double load" technique was as follows: both compartments of the cell were filled with the same solution. Samples were taken at 5 minute intervals until no further decrease in the concentration was detectable. The solute concentration in Compartment A was then raised by exchanging 5 ml of equilibrated solution with 5 ml of slightly more concentrated solution. Permeation measurements were made as described above. Permeability coefficients and rejections calculated from equation (5) for selected compounds are given in Table 3.

2.3 DISTRIBUTION MEASUREMENTS

Distribution coefficient measurements were made only with cellulose acetate membranes. The values were determined by equilibrating cellulose acetate membranes in aqueous solutions of various solutes. Changes in solute concentration in solution upon addition of membrane were determined by total carbon (TC) analysis.

The exact procedure was as follows: flat sheet dense or asymmetric cellulose acetate membranes, in quantities of 0.3 - 0.5 g, were added to 10 ml aqueous solutions containing either 25 ppm or 75 ppm of the solute. These solutions were contained in 15 ml glass vials with aluminum caps. The membranes were equilibrated with the solution for a time period of one week while constant shaking was maintained. Triplicate samples were run for each solute. Prior to the equilibrating experiments, the membrane samples had been rinsed with several changes of freshly distilled water for a time period of one month to insure that no organic solutes from the casting procedure were left in the membranes. Triplicate samples of the membranes, equilibrated with 10 ml of water for one week, served as references for the absorption measurements. (Generally the increases of organic carbon in water as a result of membrane organic elution were less than 15% of the total organic carbon of the distilled water, which was found to be 1-5 ppm.) The decrease of solute concentration as a result of membrane absorption was determined by an Ionics Total Carbon Analyzer, which enabled determination of the inorganic and organic carbon separately.

A sample calculation of S, the distribution coefficient, is shown below for the solute acetophenone. Values for the parameters of equations (9) and (6) are given in tabular form.

SAMPLE CALCULATION OF DISTRIBUTION COEFFICIENT S

Solute = acetophenone

$(Wt)_o^s$ = Weight of solute in water (ppm) = 52

$(Wt)^m$ = Weight of membrane equilibrated in water (g) = 0.328

$(Wt)^w$ = Weight of water solution (g) = 10

$(Wt)_{eq}^s$ = Weight of solute in water after equilibration with the membrane (ppm) = 25

$$(Wt)_o^s - (Wt)_{eq}^s = (Wt)_m^s \qquad (9)$$

$(Wt)_m^s$ = Weight of solute absorbed into the membrane (ppm)

= 27

$$S \text{ (distribution coefficient)} = \frac{(Wt)_m^s}{(Wt)^m} \times \frac{(Wt)^w}{(Wt)_{eq}^s} \qquad (6)$$

$$= \frac{27.10}{0.328 \times 25}$$

$$= 32.9$$

Each calculation of S requires measurements of two different blank samples by carbon analysis for the following values:

1. The weight of organic carbon in the water used to prepare the solution must be measured to obtain a correct value of $(Wt)_o^s$.
2. Pure water $(Wt)^w$ with membrane $(Wt)^m$ must be measured parallel to the sample measurement, to detect the amount of organic carbon which is discharged from the membrane. This value must be considered in the determination of $(Wt)_{eq}^s$. Three such blanks were run parallel to each S measurement.

TABLE 3 PERMEABILITY COEFFICIENTS AND CALCULATED REJECTION COEFFICIENTS

(R was calculated from equation (5) for ΔP = 54.4 atm.)

Class & Compound	Ethyl Cellulose		Cellulose Acetate		Polyurea (NS-1)	
	$\bar{p} \times 10^5$ cm/sec	R	$\bar{p} \times 10^5$ cm/sec	R	$\bar{p} \times 10^5$ cm/sec	R
ACID						
Adipic Acid	--	--	--	--	1.58	.965
Benzene Sulfonic Acid	0.01	.999	0.01	.999	1.22	.972
Benzoic Acid	0.35	.994	0.15	.995	1.06	.976
Butyric Acid	18.9	.742	8.43	.792		
Octanoic Acid	--	--	--	--	3.25	.930
ALCOHOL						
Allyl Alcohol	--	--	--	--	3.89	.917
Butyl Alcohol	--	--	--	--	1.36	.969
Resorcinol	--	--	--	--	2.04	.955
ALDEHYDE						
Furaldehyde	19.4	.737	20.5	.610	4.00	.915
Gluteraldehyde	0.01	.999	0.01	.999	2.88	.937

Class & Compound	Ethyl Cellulose		Cellulose Acetate		Polyurea (NS-1)	
	$\bar{p} \times 10^5$ cm/sec	R	$\bar{p} \times 10^5$ cm/sec	R	$\bar{p} \times 10^5$ cm/sec	R
AMIDE						
Acrylamide	--	--	14.3	.692	1.28	.971
Dimethylhydantoin	--	--	--	--	7.5	.851
AMINES						
Aniline	19.6	.735	15.8	.670	2.9	.937
Allyl Amine	--	--	--	--	9.76	.815
Ethylene Diamine	2.0	.965	1.36	.959	--	--
AROMATIC						
Benzene	26.2	.673	21.9	.594	8.15	.841
Chlorophenol	9.69	.849	14.9	.683	9.88	.813
Dimethyl phthalate	9.52	.851	6.27	.837	1.42	.968
Naphthalene	--	--	5.87	.845	--	--
Phenol	20.5	.726	16.8	.656	4.25	.910
Pyridine	9.55	.850	17.3	.650	2.07	.954
O-xylene	--	--	7.85	.803	--	--

Class & Compound	Ethyl Cellulose		Cellulose Acetate		Polyurea(NS-1)	
	$\bar{p} \times 10^5$ cm/sec	R	$\bar{p} \times 10^5$ cm/sec	R	$\bar{p} \times 10^5$ cm/sec	R
KETONE						
3-Pentanone	15.4	.779	18.6	.633	1.94	.957
NITROSO						
N-Nitroso Diethylamine	--	--	--	--	1.2	.973
MISCELLANEOUS						
Acrylonitrile	--	--	25.9	.553	15.9	.730
Methyl methacrylate	26.6	.672	14.6	.687	0.772	.982

If a wet asymmetric membrane is used for measurement, correction must be made for $(Wt)^w$. For example, the asymmetric cellulose acetate membrane used in this study was measured to contain 58% by weight free water in its porous structure. This additional water must be added to $(Wt)^w$ in equation (6). To find the weight of free water in asymmetric membranes one must weigh the wet membrane and subtract from its weight the weight of the dry membrane and the weight of the water which is dissolved in the polymeric matrix. The weight of water dissolved in the polymeric matrix is known from the solubility of water in cellulose acetate. For the sample reported here the solubility is 13.5% by weight. Thus:

Wt free water = Wt wet asymmetric membrane - (Wt dry asymmetric membrane + .135 Wt dry membrane)

Values of the distribution coefficients of selected compounds measured for cellulose acetate are reported in Table 4. The solubility parameters of the solutes were taken from reference 14 . (For correlation of the solubility parameters with the distribution coefficients, see discussion in Part II, Chapter 4.

TABLE 4 DISTRIBUTION COEFFICIENT AND SOLUBILITY PARAMETERS FOR SEVERAL WATER SOLUTES

	Distribution Coefficient S		Solubility Parameters		
Solute	25 ppm	75 ppm	δ_p	δ_h	$\delta_{ph} = (\delta_p^2 + \delta_h^2)^{\frac{1}{2}}$
Ethylene Glycol	5.5	4.5	5.4	12.7	13.8
Acetophenone	38.5	42.5	4.2	1.8	4.57
Furaldehyde	5.7	5	7.3	2.51	7.72
Ethyl Methyl Ketone	1	1	4.4	2.5	5.1
Butanol	2.5	2	2.8	17.7	8.2
Dimethylphthalate	19	18.6	5.3	2.4	5.8
Bis Chloro Ethyl Ether	28	27	4.4	2.8	5.2
Glucose	11.8	11	-	-	13.95*
Acrylamide	2.5	3	-	-	-
Xylene	56	54	0.5	1.5	1.6
Phenol	-	38	2.9	7.3	7.45

* Calculated from Hildebrand - δ

2.4 HYDRAULIC PERMEABILITY

Characterization of the specific hydraulic permeability constant of the membrane is obtained by measuring the water flux as a function of applied pressure. The measurement was performed in a cell consisting of a 50 ml water reservoir over a 15.95 cm^2 circular screen support upon which the membrane rests. A pressure of 20 psi is applied and the rate of water transport is followed by monitoring the effluent water in a 5.00 ml burette connected to the posterior chamber supporting the screen. Calculation of the hydraulic permeability constant (L_p) for the cellulose acetate membrane is given below. Measured L_p's are given in Table 5.

SAMPLE CALCULATION HYDRAULIC PERMEABILITY CONSTANT L_p

A = membrane area = 15.96 cm^2

ΔP = pressure applied = 20 psi = 1.36 atm

t = 600 sec

J = flux of water ($g/cm^2 sec$)

G = weight of transported water

$$J = L_p \Delta P \tag{2}$$

$$J = \frac{G}{At} = \frac{1.3 \times 10^{-1}}{15.95 \times 600} = 1.35 \times 10^{-5} \ g/cm^2 sec$$

$$L_p = \frac{J}{\Delta P}$$

$$= \frac{1.35 \times 10^{-5}}{1.36} = 0.992 \sim 1 g/cm^2 sec \ atm$$

TABLE 5 HYDRAULIC PERMEABILITIES OF MEMBRANES USED IN OSMOTIC CONCENTRATION

Membranes	$Lp \times 10^5$ g/cm^2-sec-atm
Cellulose Acetate	1.0
Ethyl Cellulose	0.59
NS-1 (Polyurea)	0.79

2.5 REVERSE OSMOSIS MEASUREMENT

A simple laboratory Reverse Osmosis unit is shown in Figure 2. The solution is placed in the cell and is compressed toward the membrane by gas pressure. Teflon-coated magnetic stirrers are used to mix the solution to avoid concentration buildup of solute near the membrane surface. An improved RO unit is shown in Figure 3. Here the solution flows over the membrane. This arrangement more efficiently solves boundary layer problems which occur because of solute concentration buildup near the membrane surface. (For more information on the RO unit see reference 15.)

The membrane must be conditioned to achieve equilibrated compaction before the actual measurements are made. To condition the membrane it is subjected to pure water pressure 20% higher than the upper pressure limit of the actual concentration run. After 1-2 hours the water is replaced by the solution. Samples of the solution are taken during the concentration process so that the behavior of the system can be monitored with regard to changes in concentration and rejection in relation to concentration buildup of solute, ionic strength, etc. The reverse osmosis results were taken from the literature and are reviewed in Appendix C.

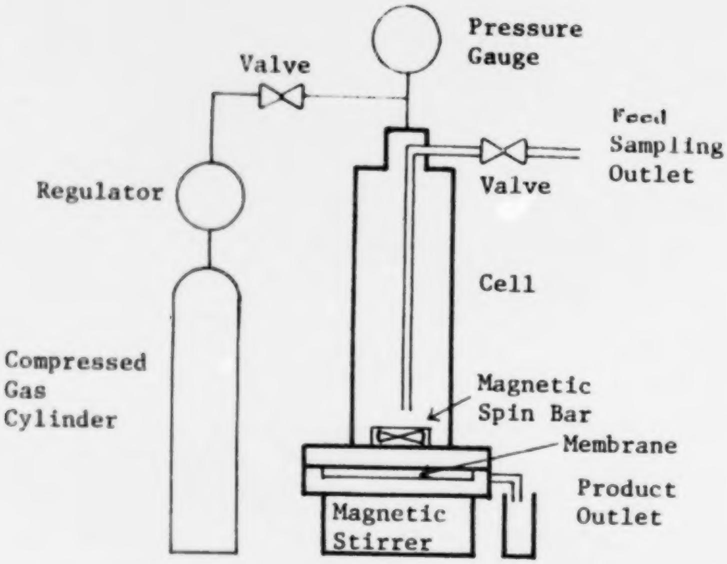
Pressure
Gauge
Valve
Feed
Sampling
Outlet
Valve
Regulator
Cell
Compressed
Gas
Cylinder
Magnetic
Spin Bar
Membrane
Product
Outlet
Magnetic
Stirrer

Figure 2

REVERSE OSMOSIS CELL ASSEMBLY, MAGNETICALLY STIRRED FEED SOLUTION

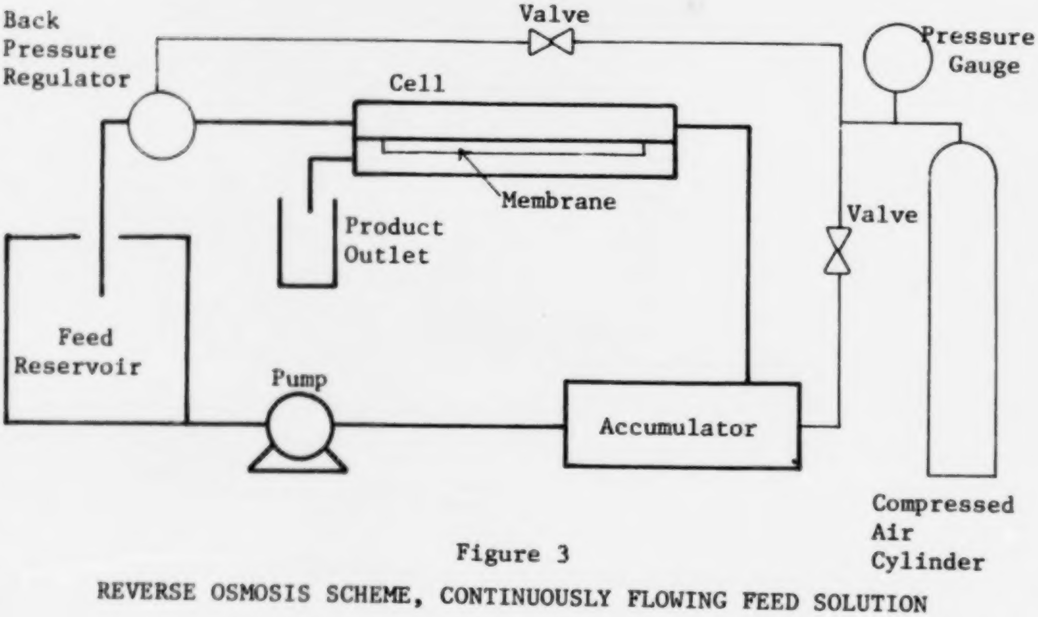
Back
Pressure
Regulator
Valve
Pressure
Gauge
Cell
Membrane
Product
Outlet
Valve
Feed
Reservoir
Pump
Accumulator
Compressed
Air
Cylinder

Figure 3

REVERSE OSMOSIS SCHEME, CONTINUOUSLY FLOWING FEED SOLUTION

2.6 OSMOTIC ULTRAFILTRATION

Osmotic ultrafiltration tests were performed in an apparatus designed and constructed at GSRI (Figure 4). A more complete, larger version has subsequently been constructed for the Water Supply Research Laboratory, Environmental Protection Agency, Cincinnati, Ohio (Figure 5). The central portion of the device is a membrane holder capable of holding membranes with effective area of 47.9 X 21.4 cm. It is arranged so that multiple flow channels are provided for alternate compartments of pump solute and sample. The membrane holder can be operated with only a single membrane in place, or with as many as 25 membranes to provide more rapid water transfer across the increased area. Pressure differences across each sheet of membrane are minimized by the routing of the solutions, and by baffle plates which support the membrane and promote turbulence (Figures 6 and 7).

A traverse across the central cell loaded with 3 sheets would identify the following layers:

1. End plate;
2. Water channel spacer and turbulence promoter;
3. Membrane;
4. Spacer to channel osmotic pump solution and turbulence promoter;
5. Membrane;
6. Repeat of (2);
7. Membrane;
8. Repeat of (4)

The water compartment and the "pump" compartment are essentially mirror images of each other; a description of one compartment thus defines the entire system. The water to be concentrated is stored in a graduated reservoir during the experiment. A peristaltic pump circulates the solution from the reservoir through the cell, via a ball type flowmeter.

A sample port and a tee to a differential manometer intersect the flow between pump and membrane holder. From the main cell, the water is returned to the original reservoir. The tubings are either all glass or steel; the reservoirs are stirred with either Teflon or steel stirrers. The only material surfaces available for absorption, i.e. loss of solute, are the plastic materials such as the polyethylene spacers. Teflon spacers also were prepared but have not yet proved feasible. The Teflon material is relatively hard, and loading the apparatus with more than two membranes creates leakage problems that are difficult to overcome. This problem is still under study. However, the areas of the tubing and spacer represent a minimal surface area in comparison to the membrane area.

Two units having different surface areas for transport have been used in the laboratory. The first, a smaller unit, used a 95.7 cm^2 area; the second, a larger unit, utilized a 1,025 cm^2 area per sheet. Total hold-up volume in the large unit is 252.8 cm^3 in the membrane compartment, and a total of 345 ml including dead volume in the pump, lines and flowmeters when a single membrane is loaded into the cell.

The design of the spacers makes possible selective channeling of either water or salt between any two membranes within the cell pack. Examination of Figure 7 will reveal the principle of operation of the spacers. Water is picked up from the entry port and delivered to channels in the common spacer which in turn deliver the water directly to the surface of the membrane.
Since the membranes are cut to the external dimensions of the spacers, the membranes themselves act as gaskets to isolate salt and water streams from each other.

For the operational study of the osmotic ultrafiltration device, see Appendix A. For concentration results see section 3.2.

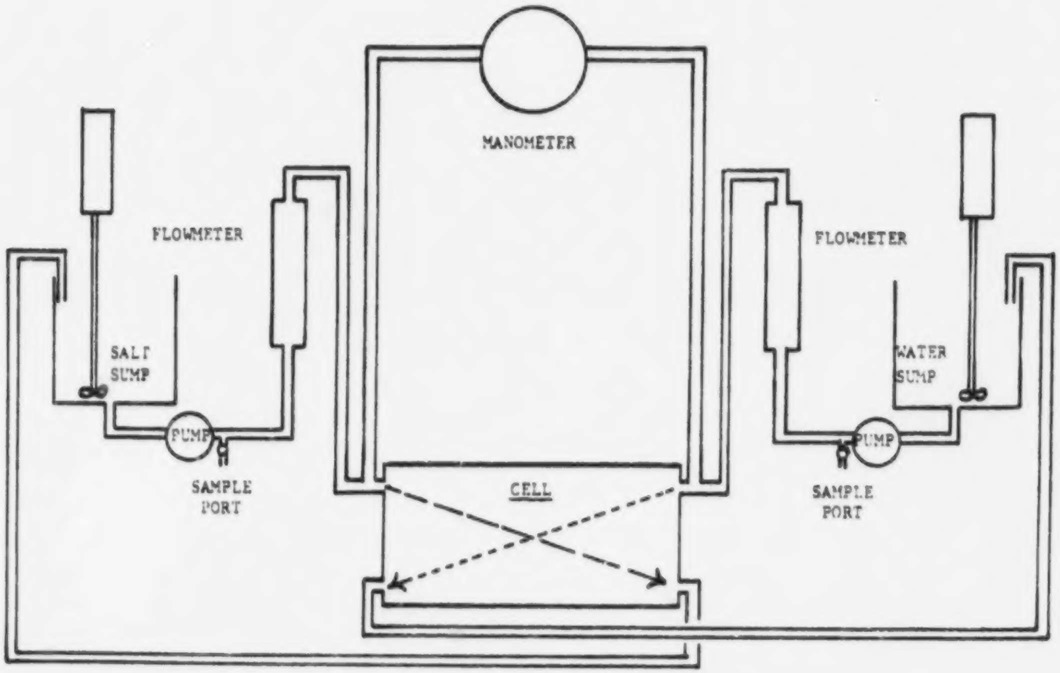
MANOMETER
FLOWMETER
SALT SUMP
PUMP
SAMPLE PORT
CELL
FLOWMETER
WATER SUMP
PUMP
SAMPLE PORT

Figure 4: Schematic of osmotic concentration system.

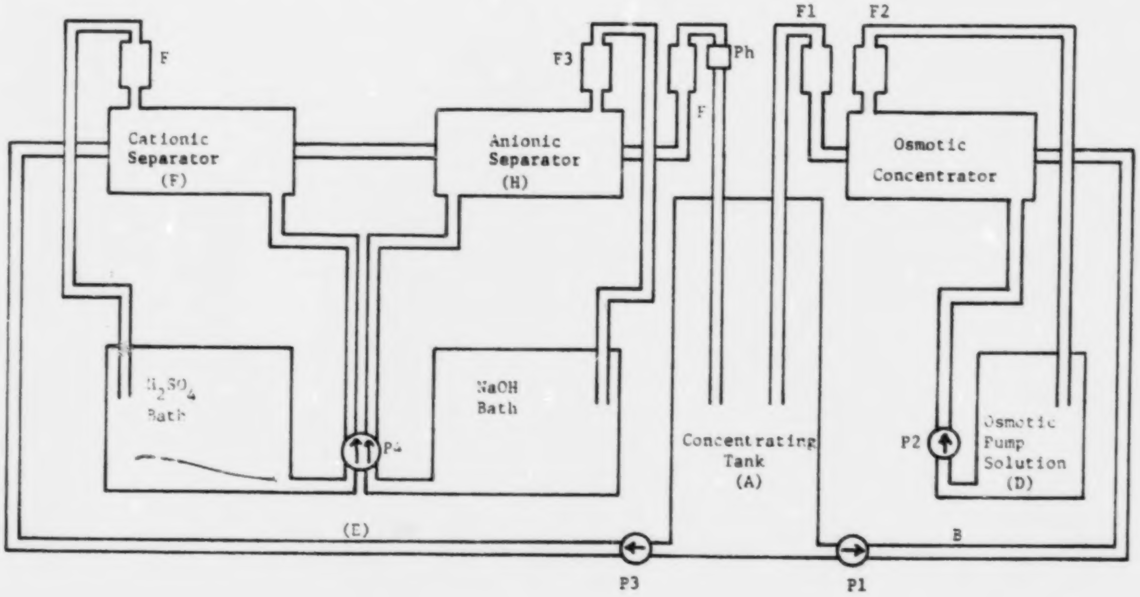
F
Cationic
Separator
(F)
F3
Anionic
Separator
(H)
F
Ph
F1
F2
Osmotic
Concentrator
H_2SO_4
Bath
NaOH
Bath
P4
Concentrating
Tank
(A)
P2
Osmotic
Pump
Solution
(D)
(E)
B
P3
P1

Figure 5: Schematic of osmotic concentrator containing Donnan softening device.

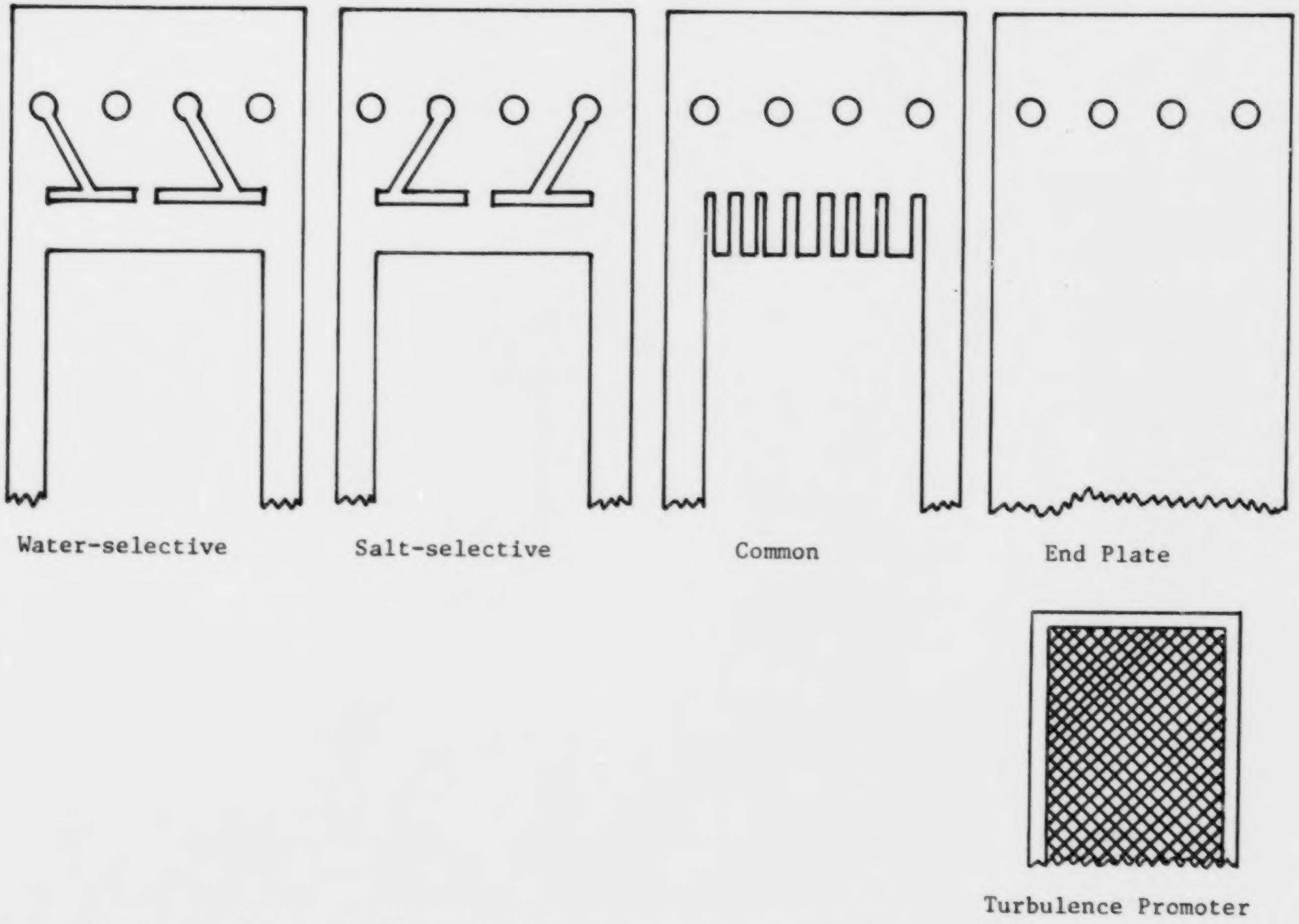
Water-selective
Salt-selective
Common
End Plate
Turbulence Promoter

Figure 6: Basic constituents of osmotic concentration cell.

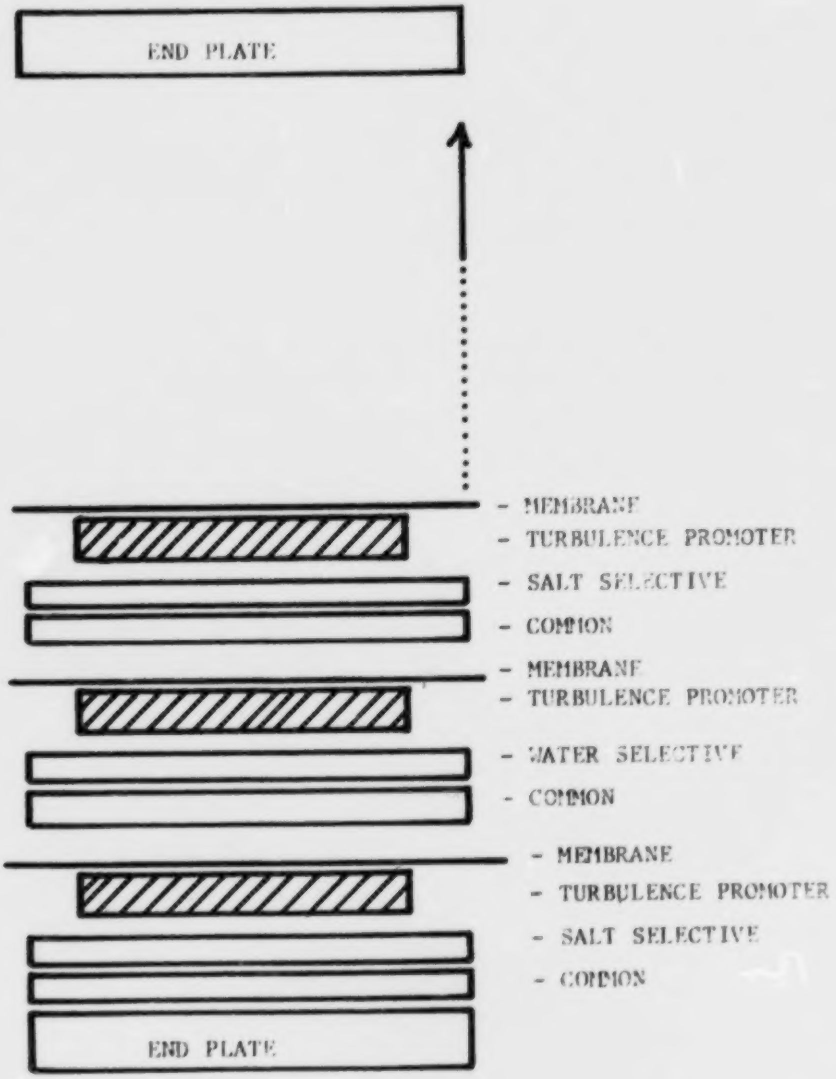
END PLATE
- MEMBRANE
- TURBULENCE PROMOTER
- SALT SELECTIVE
- COMMON
- MEMBRANE
- TURBULENCE PROMOTER
- WATER SELECTIVE
- COMMON
- MEMBRANE
- TURBULENCE PROMOTER
- SALT SELECTIVE
- COMMON
END PLATE

Figure 7: Basic constituents of osmotic concentration cell.

3.0 RESULTS AND DISCUSSION

Recent publications (Appendix C) provide substantial data on the rejection of organic solutes in water by reverse osmosis membranes. Most of the published work has been directed toward water purification. However, data relevant to the concentration of organic solutes can be extracted from these publications. A literature review including tabulation and correlation of the rejection data is reported in this section. The rejection is correlated with the permeability coefficient $\bar{p}$, the distribution coefficient S, and the osmotic concentration runs.

3.1 REJECTION OF ORGANIC SOLUTES BY RO MEMBRANES

Tables in Appendix C screen several hundred rejections reported in 17 publications. These tables include data on several varieties of the cellulose acetate membrane, four varieties of NS-1 membrane, a cellulose acetate butyrate membrane, and a DuPont polyamide membrane. Much of the information reported for the cellulose acetate membrane was measured by Matsuura and Sourirajan (16-21). These authors did a remarkable job of screening the rejection of almost all important classes of organic compounds. Also helpful is the recent work of Chian and Fang (22), who screened and compared the other membranes mentioned above. In reviewing the data included in Tables 1-4, App. C, we encountered a problem in that many of the rejection values reported in the literature were expressed graphically in figures rather than in tabular form.
Thus rejection data reported in these tables for the various organic compounds were extrapolated from figures when precise rejection values could not be found in the cited sources. This may have introduced a deviation or error of ±2% from the true rejection measured by the investigators. However, since the subject of the present study is organic concentration rather than water purification, this deviation is acceptable. (A more precise way to express the possible deviation is [100-R%] ±2.)
Hydraulic permeability L_p, which is expressed in units of g/cm^{2}sec atm,

was in most cases calculated from the reported flux of pure water through the membrane at a given pressure. Calculations were made according to the equation $J_w = L_p \Delta P$. The variations in the L_p's for certain membranes result from different membrane casting procedures and from different treatments (e.g. annealing for cellulose acetate) employed by the reporting investigators. These variations in membrane preparation techniques lead to the reporting of different rejections for a given solute by different authors. Some solute rejections are sharply influenced by the pH of the feed solution. Data on variations in casting procedure and membrane treatment, and pH data, are given in the tables under the legend "Remarks."

In considering the rejections reported from reverse osmosis experiments, one must bear in mind that experimental procedures for the evaluation of R were in most cases the so-called "short run type" as noted by Matsuura and Sourirajan (16-21). These procedures were directed toward evaluation of those kinds of rejection that are useful for the purification of water. For some of the compounds (generally those which exhibit low permeability coefficients $\overline{p}$ and high distribution coefficients S) it is questionable whether the membrane reached equilibrium with the solution in short runs of about 2 hours. Membrane areas in the reported experiments were extremely small -- as low as 7.6 cm^2 in one case (16-21). The membrane area is a very important factor in the concentration runs, as mentioned in section 1.3.2 of this paper. Data from the osmotic concentration runs, to be given below, also illustrate the importance of membrane area.

From the data presented by Chian and Fang (22) it is obvious that some organic solutes cause inherent membrane properties to change, leading in turn to changes in L_p's and R. For example, cellulose acetate membrane, which has an initial salt rejection of 97.3% (NaCl 5,000 ppm; 102 atm), was run in a series of short term experiments while several solutes were measured one after the other. After 7 solutes were measured in a row (ethanol, i-propanol, acetic acid, formaldehyde, acetone, ethyl ether, glycerol; all at concentrations of 1,000 ppm), the salt (NaCl) rejection of the membrane was reduced to 90.1%. There can be several reasons for this decline in the rejection properties of a membrane. Factors causing reduced rejection may include plasticization of the membrane by absorbed organic solutes which were not flushed out of the membrane. This example was raised to point out that rejection data from the "short run" experiments do not necessarily project the precise conditions of organic concentration. However, polyamide membranes did not show such rejection decreases. In organic concentration, the membrane is exposed to several solutes for a relatively longer period of time, and changes in its inherent rejection properties may result, as in the above example. Nevertheless, these tables are very valuable for the relative characterization of the membranes, and for establishing a working pattern for the concentration of organic solutes suspected to be present in drinking water; this will be outlined later in this chapter.

The mechanism by which a membrane rejects the passage of certain solutes while permitting water transport is still a matter of great controversy in the cited literature. Nevertheless, some conclusions can be drawn from the data in these tables. A pragmatic solution to the problem of concentrating organics from trace levels can be achieved, even in the absence of an understanding of the underlying mechanisms. In the following discussion, the separation of organics will be treated by membrane type.

3.1.1 Cellulose Acetate

The rejection by membranes prepared from cellulose acetate is highly dependent on the method by which the membrane is prepared, and on the degree of acetylation of the starting polymer (23-24). The most commonly used polymer is a cellulose derivative in which 2.5 of the 3.0 available hydroxy groups have been acetylated. If the acetyl substitution is increased, the structures are more densely packed, and there is a decrease in solubility of water in the membrane. Paralleling this decrease, there is a general increase in the rejection performance of the resulting membranes. When the polymer with 2.5 degree of acetyl substitution is blended with a fully esterified polymer (3.0 acetyls per repeating unit), the properties are a compromise; i.e. the water flux is decreased due to lower solubility of water in the polymer, but at the same time the rejection of solutes is improved.

Raising the annealing temperature of the finished membrane has an effect similar to that of increasing the acetyl content, i.e. it lowers the hydraulic permeability, L_p, and raises the rejection, R. Consequently, the L_p value in the App. C can be used as a guide for comparing expected results. An examination of the tables shows that there is a general inverse correlation between L_p and R. For low L_p membranes, the rejection increases for a given solute. Similarly, the rejection performance of organic solutes by a given membrane preparation can be compared by examining the salt rejection properties of the membranes (page 29, Appendix C).

The rejection properties of cellulose acetate toward various kinds of organic solutes follow the trend shown in Figure 8 - 9. In general there is a correlation between the ability of the solute to form hydrogen bonds with water compared to its ability to form bonds with the membrane. Dissociated solutes, polyhydric alcohols, and the paraffins are better rejected by the membranes. The rejections of phenols in their undissociated state are extremely low; the same characteristic is observed with other organics capable of ionizing (Figure 10).

Rejection of organics increases with an increase in the degree of branching and with the number of carbon atoms for compounds having the same functional groups. However, some exceptions to this statement are known and are illustrated in Figure 11 , where the dicarboxylic acids are shown to decrease in rejection with increasing carbon number. The mechanism of permeability of organic solutes through the membrane probably involves several parameters other than molecular size and the che-

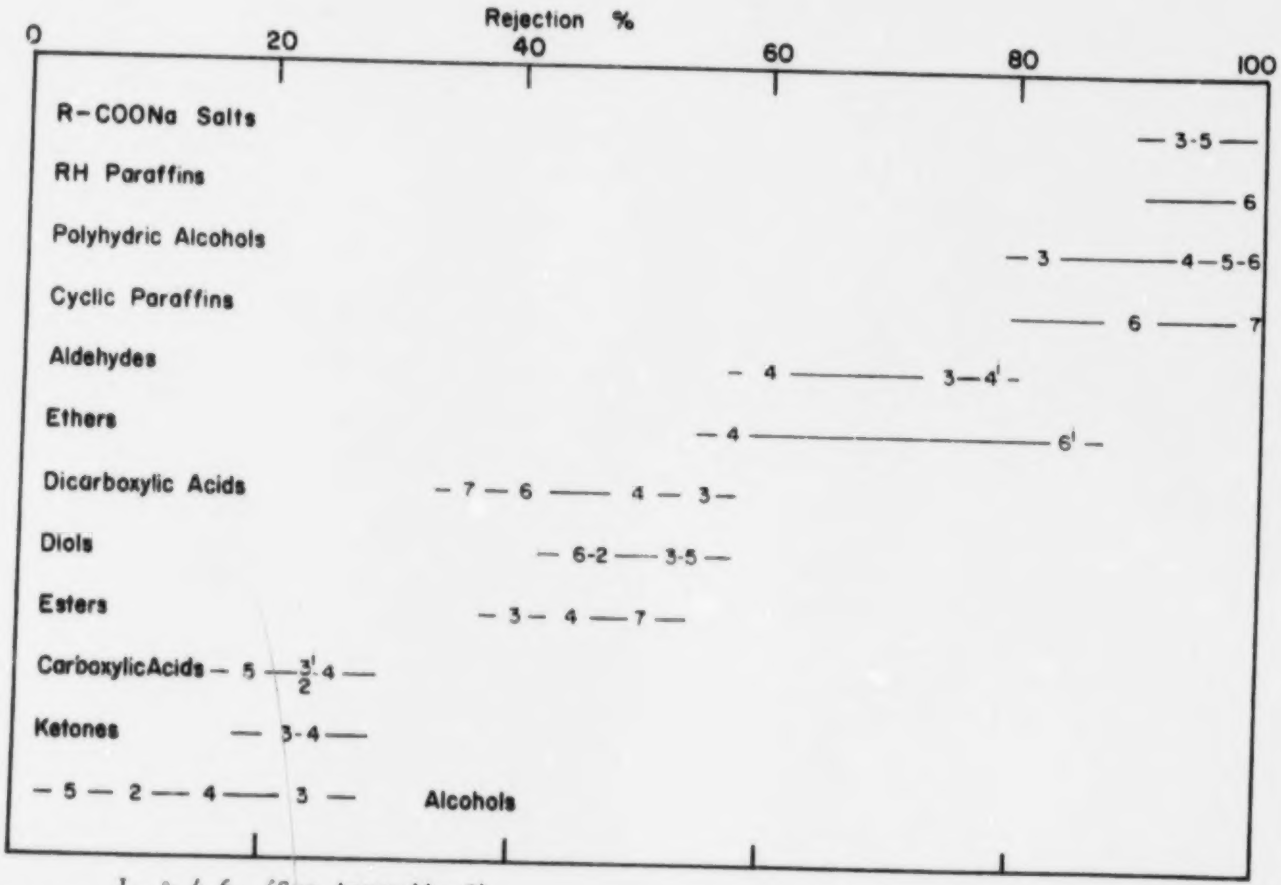

Figure 8: $L_P \sim 4.6$ (See Appendix C)
Cellulose acetate rejections of 12 classes of alkyl compounds. (Numbers denote carbon atoms in the compounds.)

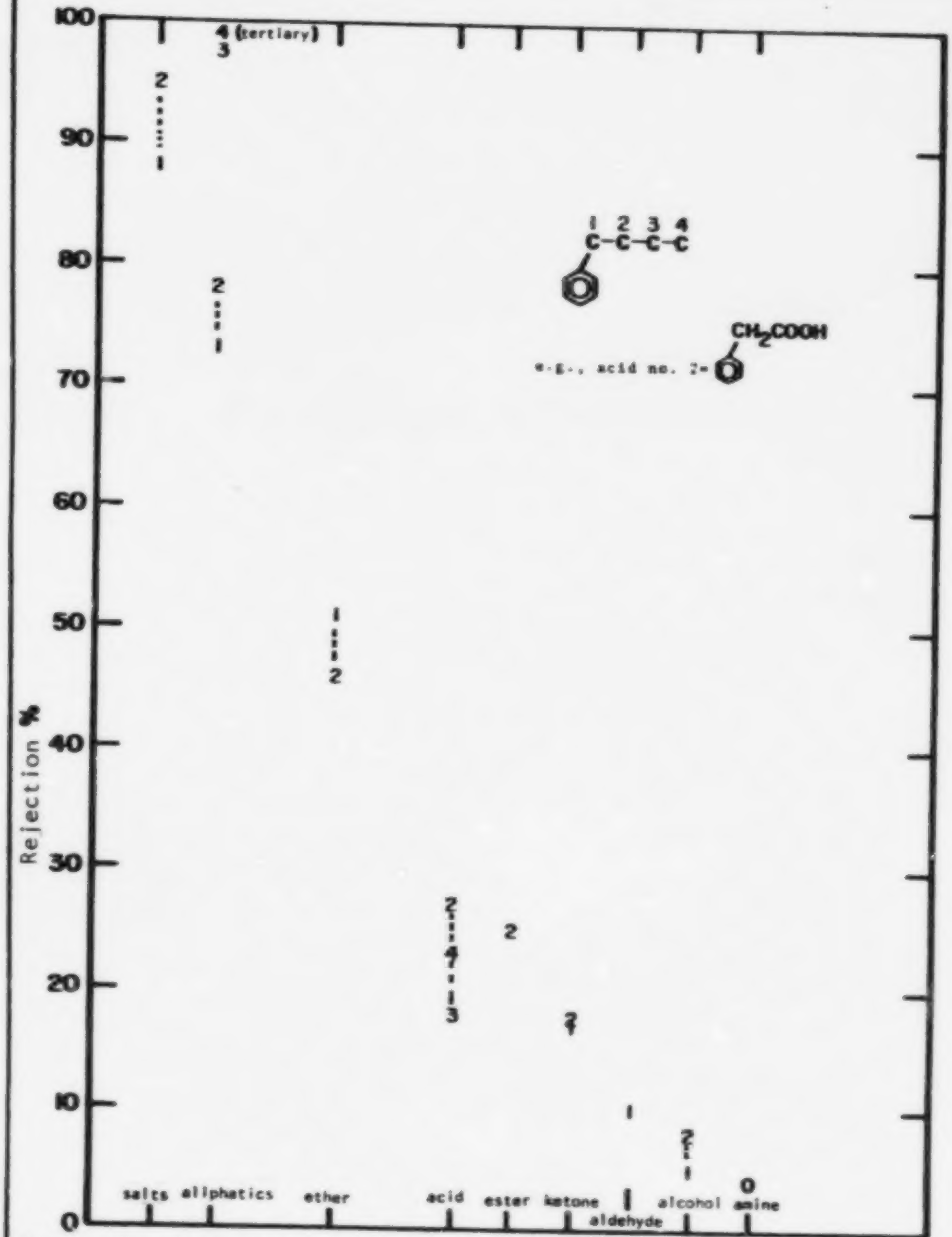

Figure 9: Rejections of 9 classes of aromatics. (Numbers denote carbon atoms in the compounds.) Cellulose acetate $L_p \sim 4.6$ (See Appendix C)

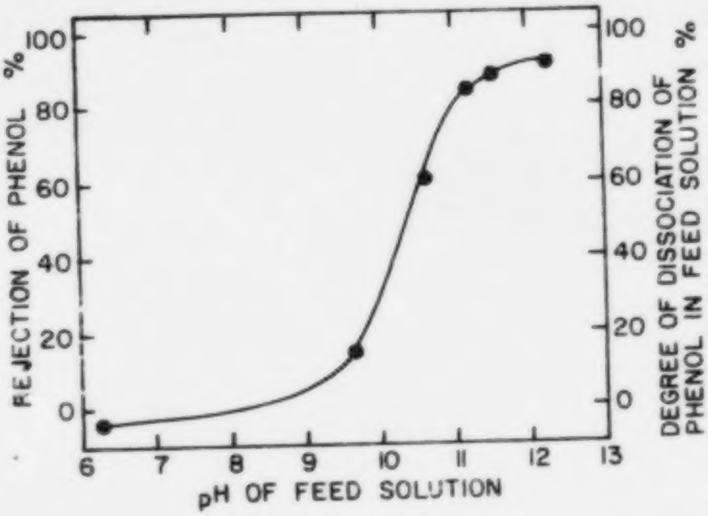

Figure 10

Cellulose acetate rejections of phenol as a function of pH

(data taken from Matsuura and Sourirajan). **Ref. 21**
$L_p \sim 4.6$
Pressure = 34 atm.

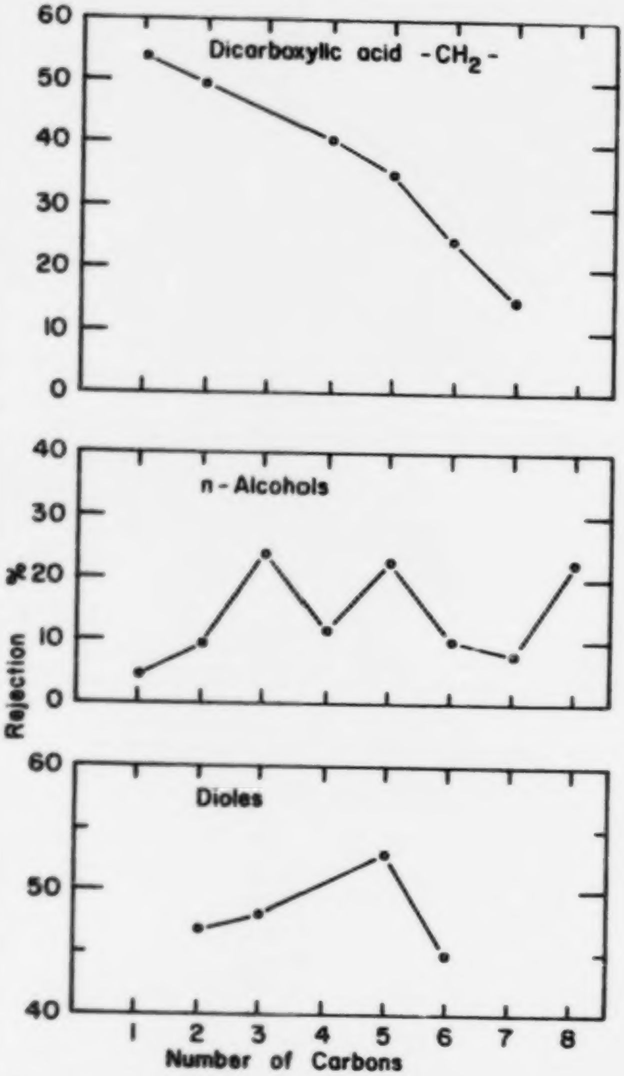

Figure 11: Cellulose acetate rejections of 3 classes of linear alkyl compounds, as a function of the total number of carbons.

$L_p \sim 4.6$

Pressure 102 atm. (See Appendix C)

mical nature of the functional groups; some of these effects will be discussed later in this report.

Membrane rejection is strongly influenced by functional groups of the solute. In Figure 9 are shown the rejections of a number of benzene nucleus derivatives, with side chains varying from one to four carbons. While the size of the molecule is reflected in the relative rejection values, the greatest influence is exerted by the nature of the functional group on the side chain. Even with an aromatic nucleus, the change from amine to ester to ether is quite dramatic.

Matsuura and Sourirajan (16-21) tried to correlate the measured rejections to solute properties as represented by Taft, Hammet, and Small numbers of the different classes of solutes. They were able to show that the infrared (IR) frequency shift of OH bonds resulting from decreased acidity correlated with increased rejections, or conversely with increased basicity (as indicated by IR band shift). While their remarkable quantity of data and correlations are valuable, one must not ignore the thermodynamic state of a three component system: membrane-water-solute. More generalized conclusions can be reached using the previously explored concepts of solubility parameters. The latter already contain within them the Hammet, Taft, and Small correlations between solubility and structure. The use of such solubility parameters will be discussed in a later section of this report.

3.1.2 NS-1 Membrane

The NS-1 membrane, prepared from an interfacial condensation between an amine and an isocyanate, evidences rejections that are much higher than those observed with cellulose acetate membranes. Such results were predictable from the solute permeabilities reported in Table 3. Rozelle (12) et al. have reported the rejections of two versions of this membrane. They classify the preparation into a "standard" and "modified" procedure. The modified procedure leads to a more highly cross-linked membrane. These procedural changes resemble somewhat the "annealing" procedures reported for cellulose acetate membranes, but in this case lead to a highly cross-linked membrane surface. The modified NS-1s have lower L_p values than the membranes prepared by the standard method and exhibit higher rejections of organic solutes.

Analysis of the data in Table 2, Appendix C for NS-1 rejections shows that increasing molecular size (for solutes of the same functional type) leads to better rejections. Such observations are in accord with the results for "modified" versus "standard" membranes, where the lowered L_p and increased rejection of the "modified" membrane are thought to result from the more dense structure. Thus it can be concluded that for this type of membrane structure the ability of a solute to permeate is a reflection of the soluts's ability to penetrate the cross-linked surface.

The higher the cross-link density, the better is the rejection. From Figure 12 one can see that the nature of the functional group is much less important in governing rejection by the NS-1 membrane than compared to the cellulose acetate membrane. The differences in the essential transport mechanism through these two kinds of membranes leads to the observed patterns of rejection behavior as a function of pressure. Figure 13 shows that increasing the pressure on a solution of p-chlorophenol results in increased rejection; the opposite trend is observed with cellulose acetate membranes. The pressure dependence of rejection is a significant factor to be considered in the practical applications of this work, and will be discussed in greater details in section 3.3.

The excellent rejection of organic solutes by the NS-1 membrane and the wide pH range over which it can operate are attractive features. However, the sensitivity of this material to chlorine (1 ppm or greater leads to reduced rejection) is an impediment to its practical utilization. The pH stability of the membrane allows operation in both acidic and basic media; this permits alteration in rejection properties of those solutes that act as Lewis bases. The polyurea structure of the membrane

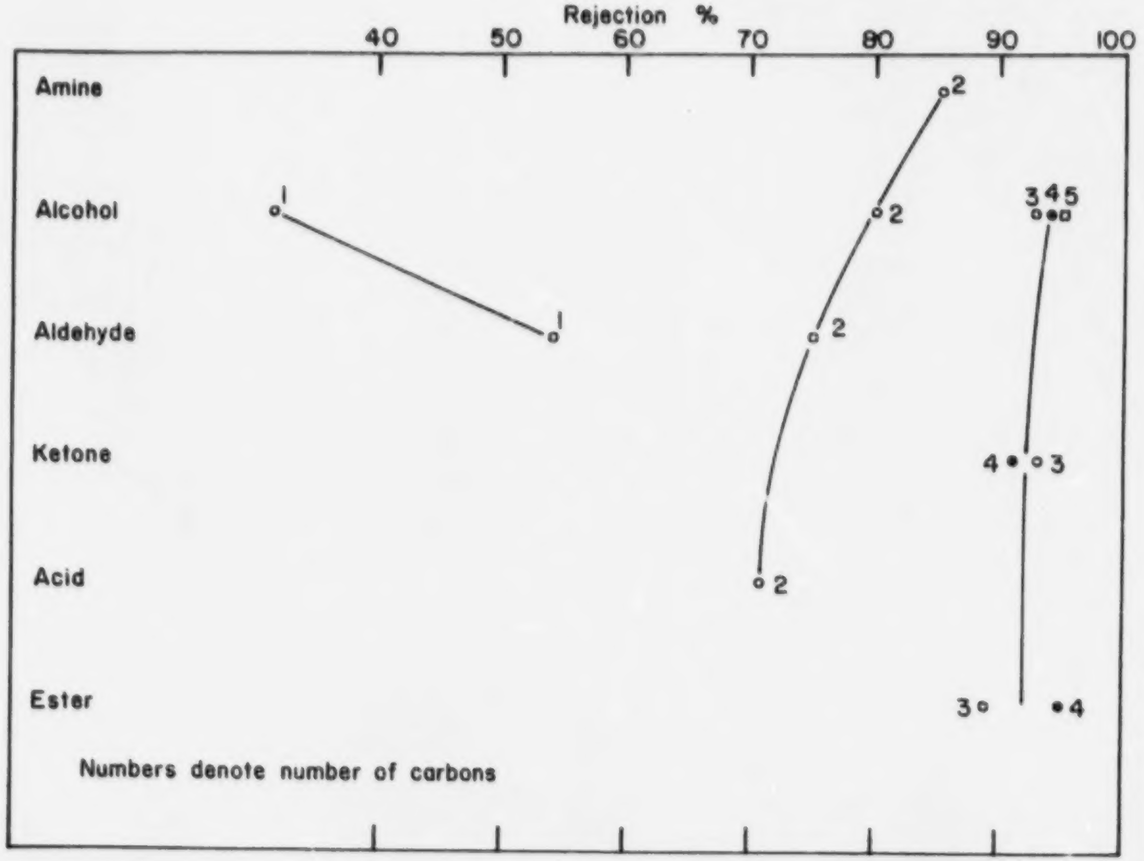

Figure 12: NS-1 rejection of 6 classes of n-alkyl compounds. (Numbers denote carbon atoms in the compounds.)

$L_p \sim 1$ Pressure 54.4 atm.

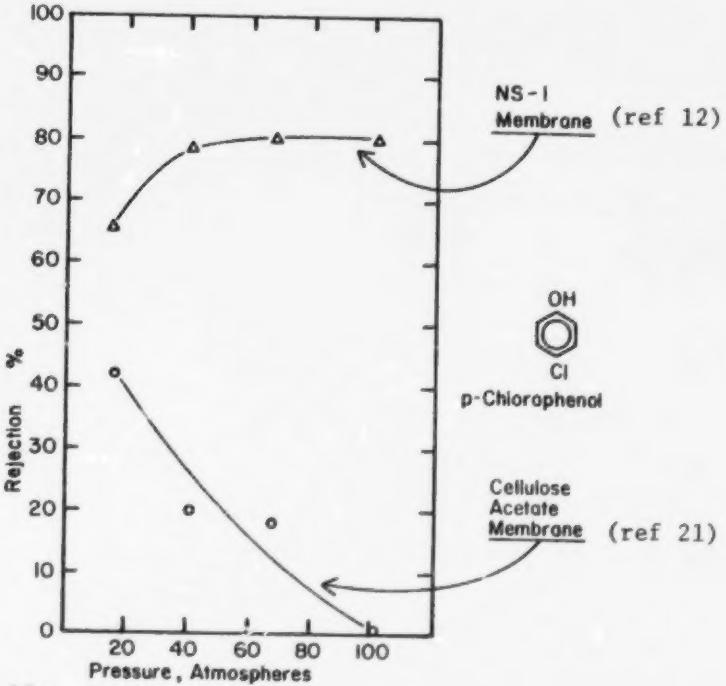

Figure 13: Rejection of p-Chlorophenol as a function of pressure with NS-1 and cellulose acetate membranes.

is protonated in solutions that have pH values below 10.8. This resembles a Lewis base characteristic of the NS-1 membrane, which explains the trend shown in Figure 12 (see the curve for 2-carbon compounds) toward higher rejections for amines than for acidic compounds.

3.1.3 Polyamide Membranes

Chian and Fang (22) tested the rejection properties of polyamide membranes toward a variety of solutes. The membranes were provided by the DuPont Co. Perma-sep Division as hollow fibers, and flat sheet membranes were supplied by Chemstrand. The rejection of the polyamide is quite similar to that observed for the NS-1 membrane (see Table 4, Appendix C, Figure 14), and it is also highly sensitive to the presence of trace levels of chlorine.

The behavior of the reverse osmosis membranes are compared in Figure 14. This figure, which represents a rearrangement of the data given by Chian and Fang (22), shows the potential separation of each membrane. (Note that from Appendix C it appears that the NS-1 membrane reported by Rozelle et al. [12] has better rejections than reported by Chian and Fang.) A working scheme for concentration can be drawn from Figure 14. For example, a set of two reverse osmosis units connected in series can be employed. The first unit will be loaded with cellulose acetate, which will retain the salts and high molecular weight products. The product stream from the first unit will feed a second unit which will be loaded with polyamide membrane. Low molecular weight solutes will be retained and concentrated by the second unit.

The results of the reverse osmosis (RO) experiments discussed in the preceding sections are not readily interpretable in terms of measurable interaction between a series of solutes and one or more membrane types. Such data are needed for development of a predictive scheme that will allow selection of membrane combinations for retention of all types of solutes. Furthermore, the nature of the RO equipment is such that a certain residual circulating volume must always be maintained in the circuit; this precludes concentrating the test samples to very small

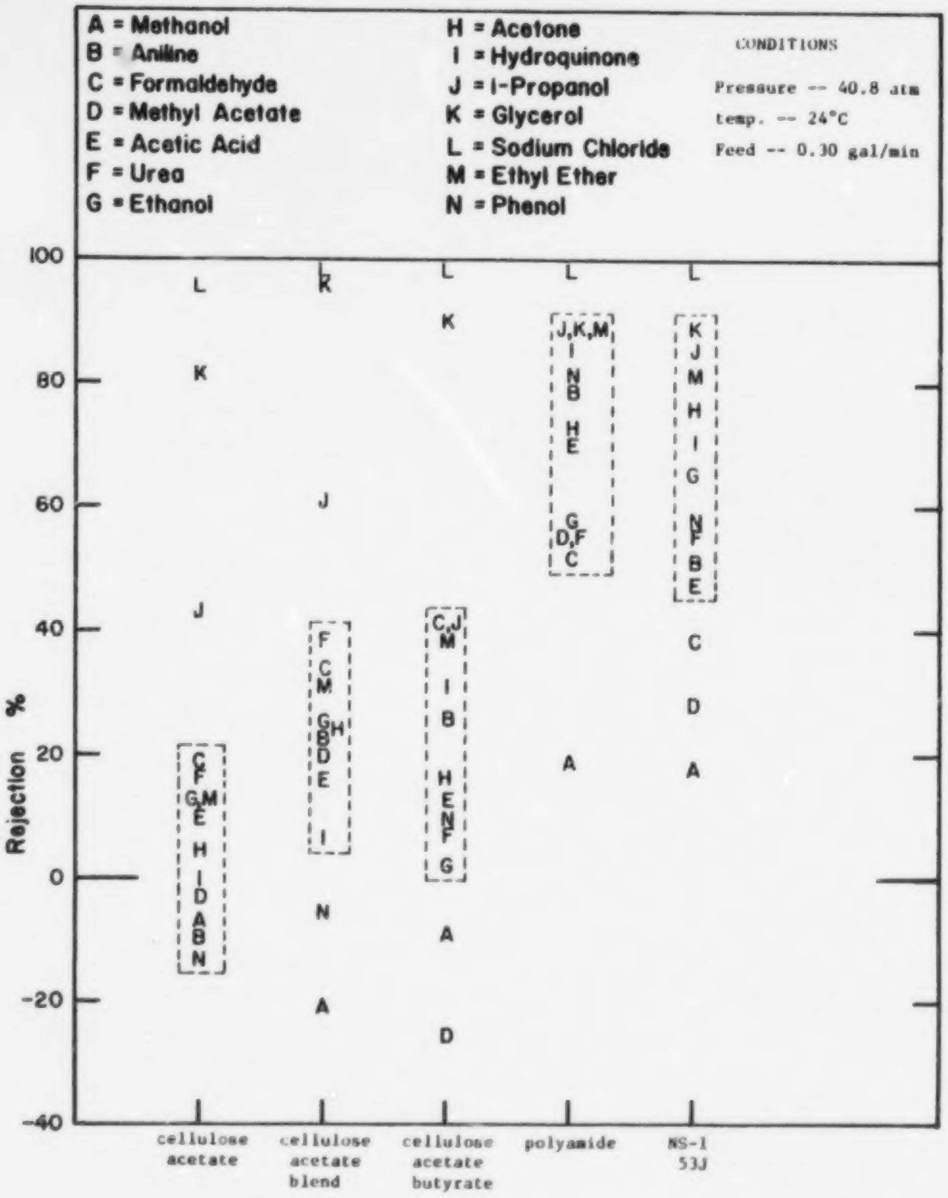

Figure 14: Rejection performance of 5 different RO membranes (data from Chian and Fang).

volumes, and to very high concentration multiples.

These two problems can be resolved if a direct correspondence can be demonstrated between the RO method and the Osmotic Ultrafiltration process described in the Introduction. To test this correspondence, a series of experiments was initiated to test the ability of the OC unit to concentrate spiked samples using the same membrane types as are employed in RO modules. Cellulose acetate was selected because of its availability, and because it responds over a wider range of permeabilities.

3.2 OSMOTIC CONCENTRATIONS OF ORGANIC SOLUTES

Concentrations of various organic solutes in water were carried out in the Osmotic Concentrator ($\overline{\mathrm{OC}}$) as described in the Experimental section of this report. All the concentration measurements were carried out with asymmetric cellulose acetate membranes. The membranes were loaded so that the "skin" side was facing the water-solute compartment (Case II, Appendix A, Figure 31).

Up to 19 liters of solutions were concentrated; the initial concentrations of the organic solutes were in most cases in the range of 25-100 ppm. All concentration runs included the following measurements:

a. Rate of water transfer;

b. Rate of concentration;

c. Organic solute buildup in the pump solution.

From these measurements the change in the osmotic pressure during the concentration run was calculated using the relation $\Delta P = J_w/AL_p$ when ΔP is effective osmotic pressure and A is the membrane area.

From the effective osmotic pressure (ΔP) and the permeability coefficient $\overline{p}$ the predicted rejection was calculated using equation (5).

$$R = \frac{L_p \ \Delta P}{L_p \ \Delta P + \overline{p}} \qquad (5)$$

The experimental rejection was calculated directly from the rejection equation (4).

$$R = 1 - \frac{C_p}{C_f} \qquad (4)$$

C_p and C_f were determined during the concentration run. (C_p was calculated from $\frac{\Delta Qn}{\Delta Vn}$; where ΔQn and ΔVn are, respectively, the total amount of solute and total volume of water which were transported from the water compartment to the pump solution in the time period Δt_n.)

The amount of salt enrichment in the water compartment, due to the transport of pump solute through the membrane, was measured also.

The concentration experiments indicate that there are two classes of organic solutes:

1. Those which obey the rule derived from the rejection equation (5) which anticipates an increase in rejection with an increase in pressure; and
2. Those which exhibit the contrary trend, a decrease in rejection with an increase in pressure. This is demonstrated in Table 6.

In the concentration run with dimethyl phthalate as a solute, we find good agreement between the experimental and predicted rejections. It can be seen that an increase in pressure leads to a substantial increase in the rejection, as is anticipated. Glutaraldehyde was found to exhibit the same trend. A different response was found when benzene sulfonic acid in the acidic form is the solute with pH = 5-6. The rejections and the pressure trends are in the opposite directions, and the agreements between the calculated and the experimental rejections are not as precise. This kind of behavior is shown in its extreme case with phenol, where negative rejection is found when high pressure is applied.

The concentrations of five organic solutes employing osmotic pumping are shown in Figures 15-21. The different solutes were chosen to illustrate a number of organic types. Polyethylene glycol is a water soluble polymer and represents the high molecular weight organics which can be found in drinking water. Bis-2-chloroethyl ether is reported to be a potentially carcinogenic low M.W. material, and is defined by us

TABLE 6 THE REJECTION OF ORGANIC SOLUTES THROUGHOUT CONCENTRATION RUNS BY CELLULOSE ACETATE MEMBRANE

SOLUTE	P (ATM.)	R-PRED.* (%)	R-EXP.** (%)
DIMETHYLPHTHALATE	4.22	40	32
DIMETHYLPHTHALATE	18.9	72	78
GLUTARALDEHYDE	21.8	99.9	99.9
FURALDEHYDE	23.3	54	12
BENZENE SULFONIC ACID	29.2	96	71
BENZENE SULFONIC ACID	23.2	99	81
PHENOL	68	27	-10

*Calculated from $R = \frac{L_p \Delta P}{L_p \Delta P + \bar{p}}$

**Calculated from $R = 1 - \frac{C_p}{C_f}$

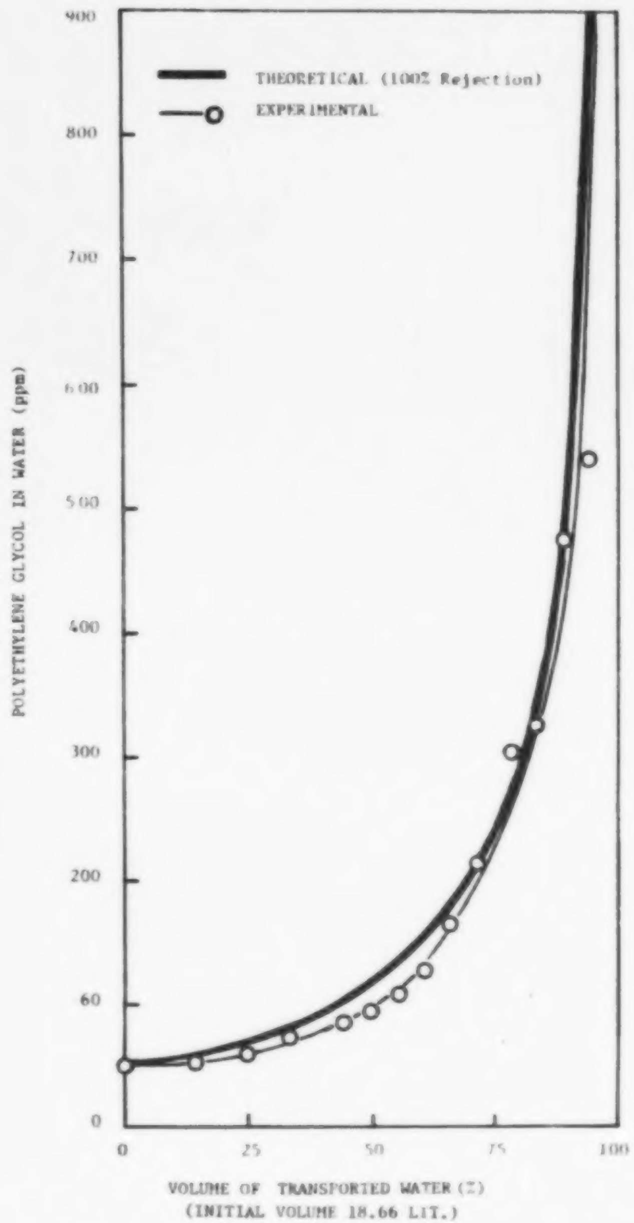

Figure 15: Osmotic concentration of polyethylene glycol (M.W. = 3000), Run C-45.

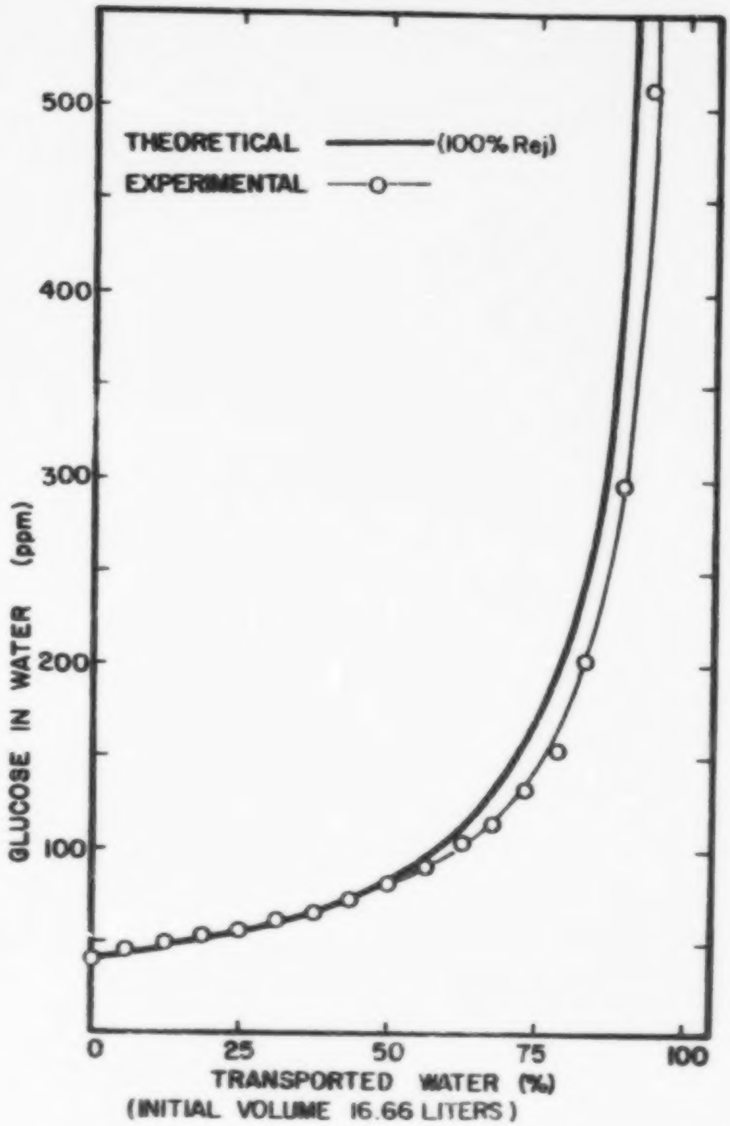

Figure 16: Osmotic concentration of glucose, Run C-43.

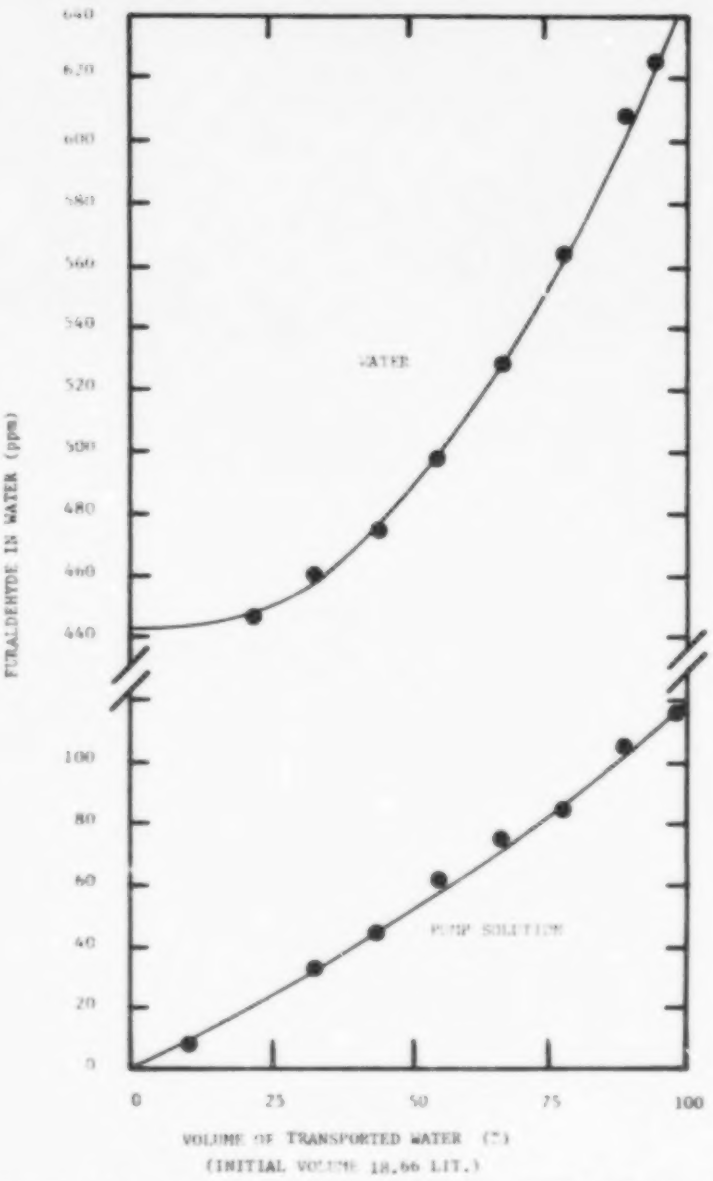

Figure 17: Osmotic concentration of furaldehyde, Run C-41.

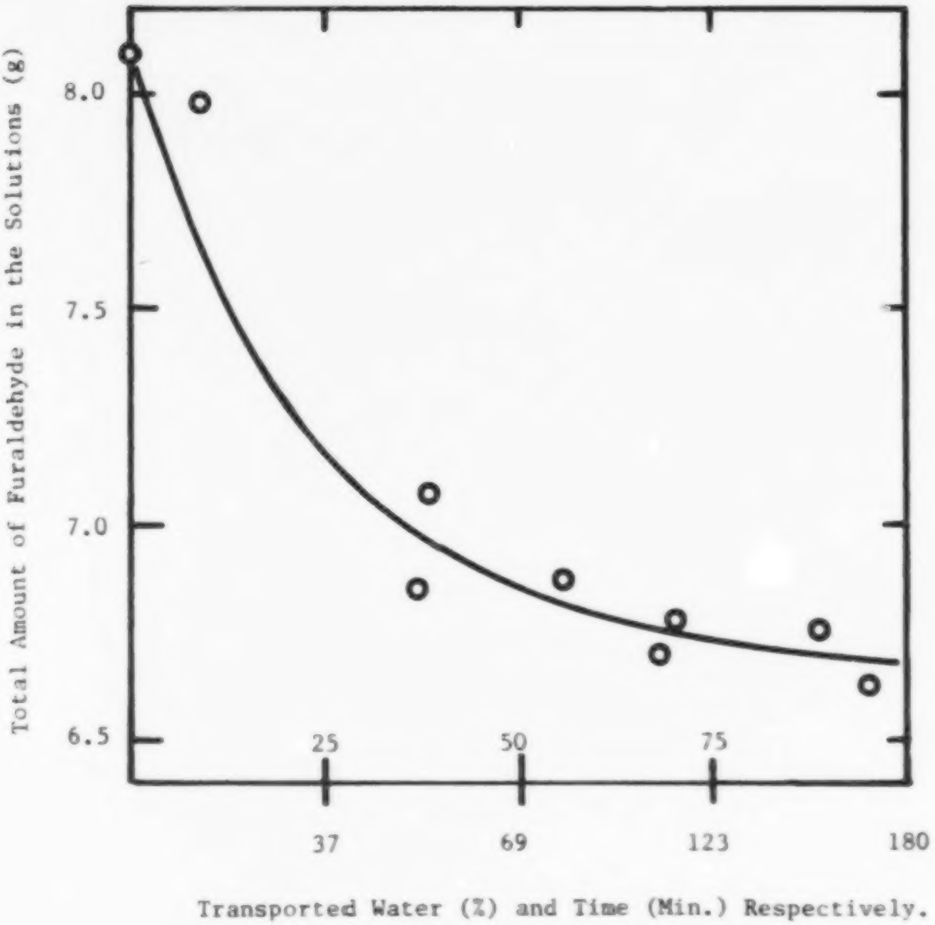

Figure 18: Mass balance of furaldehyde, Run C-41.

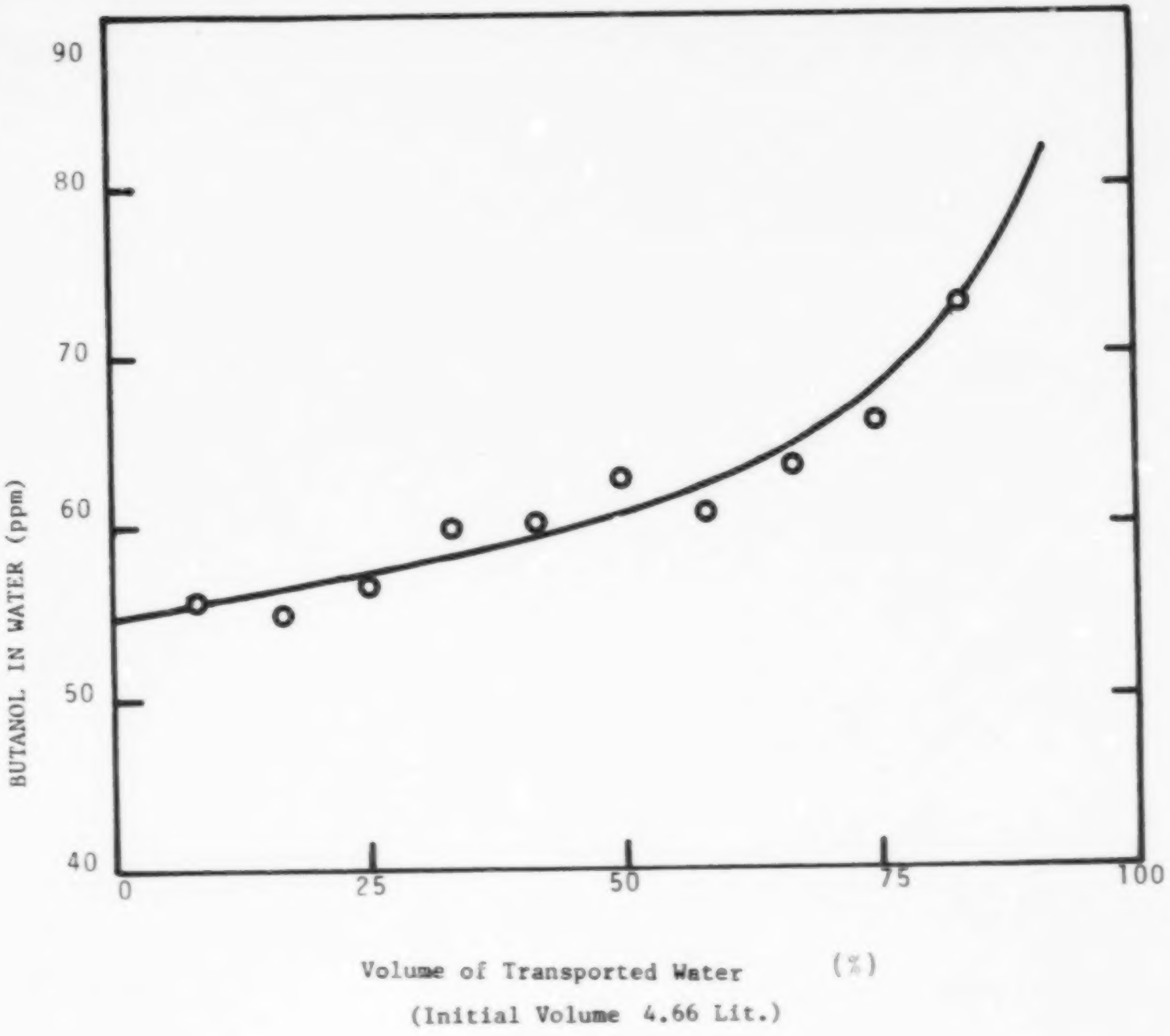

Figure 19: Osmotic concentration of n-Butanol, Run C-34.

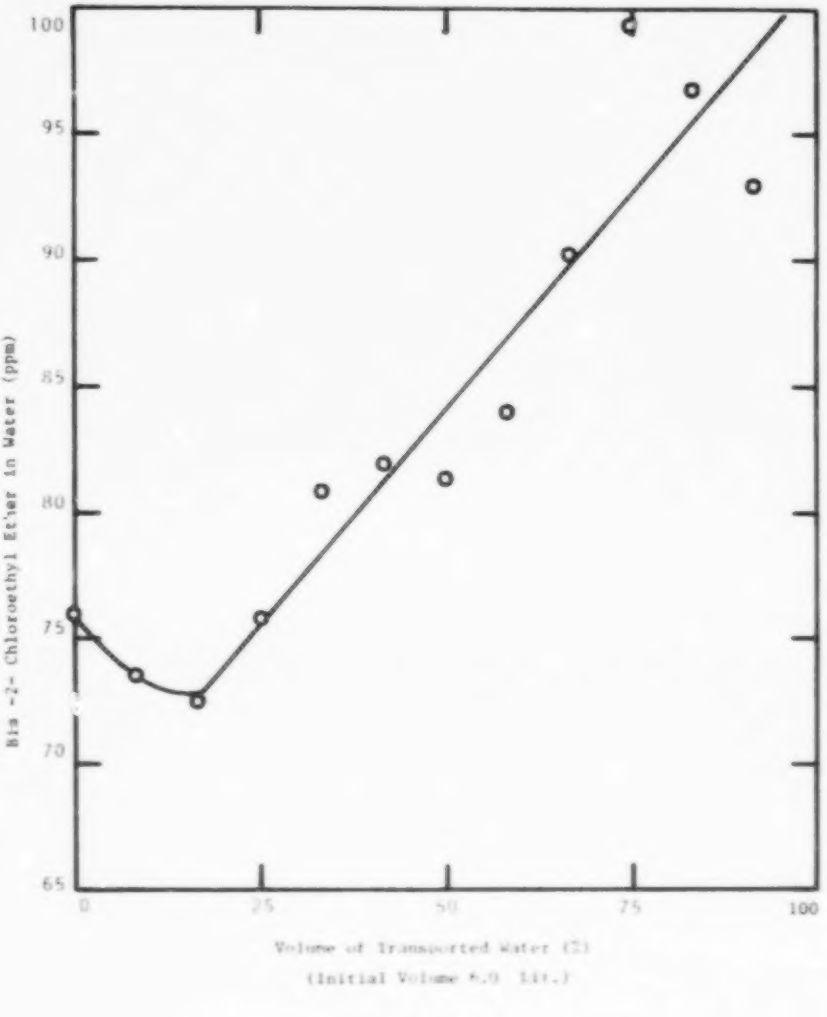

Figure 20: Osmotic concentration of Bis-2-Chloroethyl Ether, Run C-55.

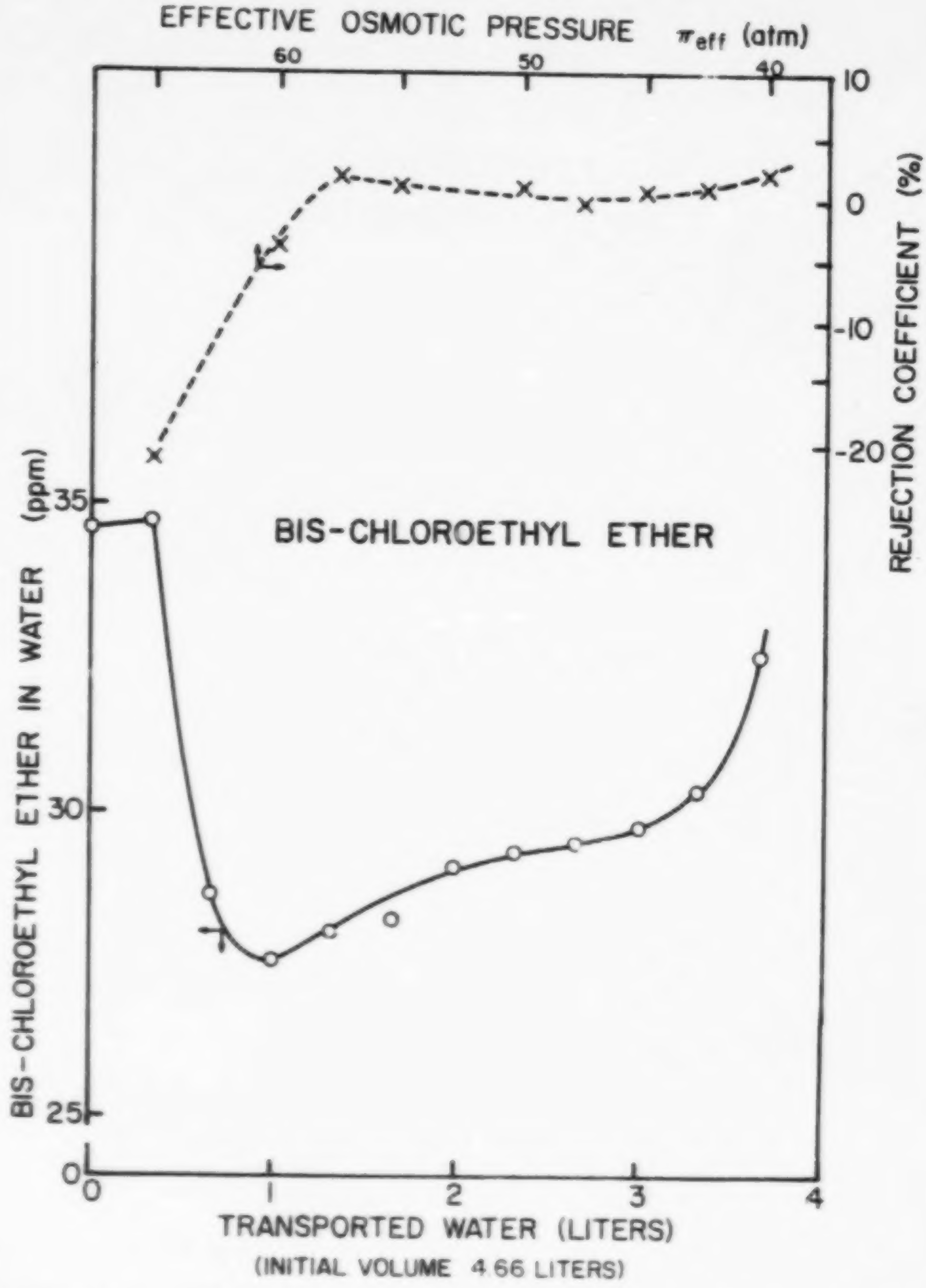

Figure 21: Osmotic concentration of Bis-2-Chloroethyl Ether, Run C-35

as water insoluble, thus exhibiting a relatively high distribution coefficient, S (see Table 4). Butanol and furaldehyde have small S values and their solubilities in water are 7.9% and 8.3% (20°C) respectively. Glucose has a high hydrogen bond capacity and is similar in structure to the membrane polymer unit. Selecting these solutes for the concentration measurements provides us with representative ranges of distribution coefficients and water solubilities.

The results of the concentration procedure can be described by two parameters:

1. The "enrichment factor" which is defined as:

$$\frac{\text{final solute concentration } (C_1)}{\text{initial solute concentration } (C_i)}$$

2. The amount of solute recovered in the water compartment at the end of the concentration step; this can be calculated from the following equation:

$$\text{Amount of solute recovered (\%)} = \frac{C_1 V_1}{C_i V_i} \times 100$$

where V_i = initial volume
V_1 = final volume

Table 7 shows the results of nine concentration runs which were carried out with the selected solutes. From the enrichment factors it can be seen that for polyethylene glycol, and glucose, the osmotic concentration process with cellulose acetate membrane is very effective and that high concentrations can be achieved. Poorer recoveries were achieved with the three other solutes.

TABLE 7 CONCENTRATION RUNS FOR FIVE ORGANIC SOLUTES

No.	Solute	Initial Volume V_i (1)	Initial Concen. C_i (ppm)	$\frac{V_i - V_1}{V_i}$ X 100	Solute Recovery $\frac{C_1 V_1}{C_i V_i}$ X 100	Enrichment Factor (C_1/C_i)	Time t(min)
C-45	Polyethylene Glycol	18.66	51	91	90	10.3	420
C-43	Glucose	16.66	38	90	82	8.28	203
C-47	Furaldehyde	18.66	60	91	12.5	1.4	163
C-41	Furaldehyde	16.66	445	(90)	(9.25)	(1.45)	147
C-57	Furaldehyde	6	25	91	10.3	1.24	480
C-37	Butanol	4.66	55	79	28	1.32	50
C-49	Bis-2-Chloroethyl Ether	16.66	68	90	15	1.5	158
C-55	Bis-2-Chloroethyl Ether	6	76	91	10	1.27	153
C-35	Bis-2-Chloroethyl Ether	4.66	35	79	20	0.93	42

Note: Membrane areas were 3075 cm^2 except for C-55 and C-57, where the area was 1025 cm^2.

From the table and figures it appears that the enrichment factor is dependent upon the initial volume to be concentrated; generally higher enrichment factors were achieved from larger initial volumes. This behavior is the result of solute absorption in the membrane and on the apparatus walls. This phenomenon is shown very clearly in the bis-2-chloroethyl ether concentration runs. This compound has a high distribution coefficient, and it is anticipated that a substantial loss of solute to the membrane will occur during the initial steps of the process. From runs C-35 and C-55, Table 7, Figures 20-21, it can be seen that a progressive decrease in C_i occurs in the first part of each of the concentration runs. Run C-35, which was operated with a large membrane area and which has the smaller C_i, did not reach the initial concentration even by the end of the run. The concentration runs of furaldehyde and n-butanol, solutes which exhibit small values of S in cellulose acetate, are not affected as much by this phenomenon; however, the mass balance of furaldehyde during the concentration experiment indicates the typical trend of loss of solute to the membrane and to the apparatus by absorption (Figure 18).

The concentration runs were conducted so that the concentration of the pump solution, and hence the effective osmotic pressure, was progressively decreased with respect to the transported water. (The initial concentration of the pump solution was not subjected to any outside control). This enabled us to measure the rejection coefficient with respect to the changes in the effective osmotic pressure. Figures 22-23 show the characteristic behaviors of the solutes in such a system. Different trends will be observed with other membranes.

Glucose, bis-2-chloroethyl ether and n-butanol exhibit increases in rejection with increased pressure; furaldehyde shows a decrease in rejection as pressure increases. For further discussion of this subject see section 3.3.

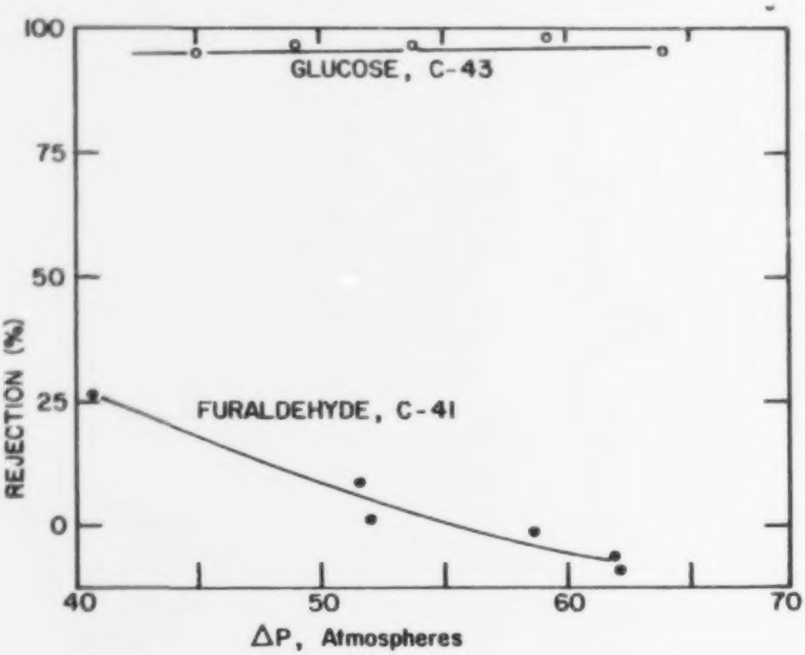

Figure 22 : Rejection of Glucose and Furaldehyde vs. effective osmotic pressure in the osmotic concentration runs C-43, C-41.

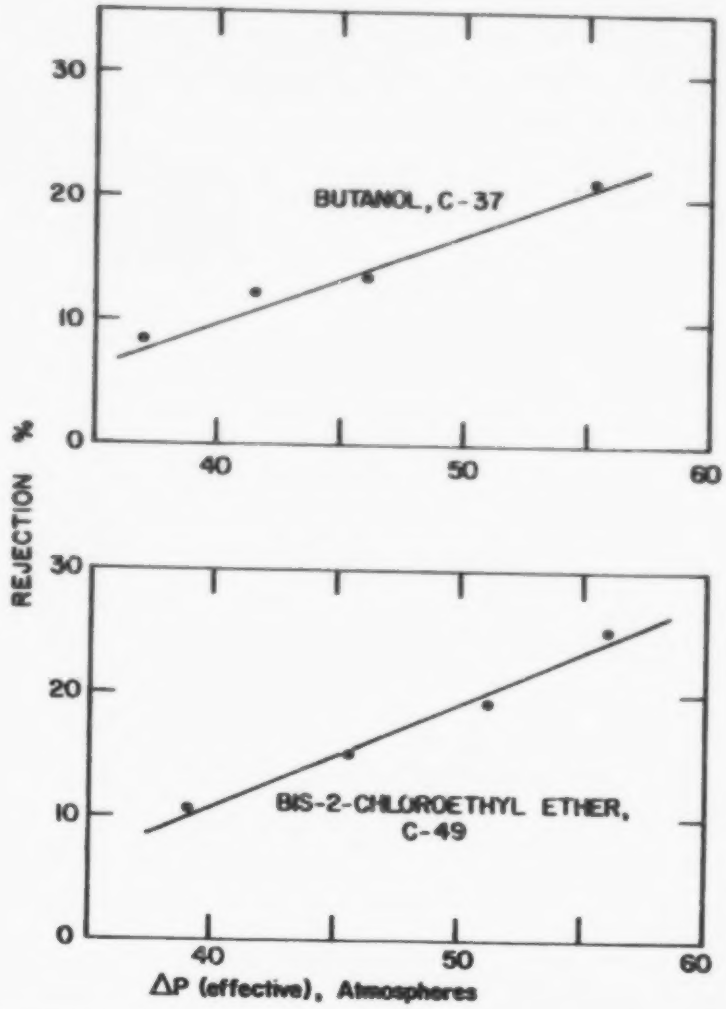

Fig. 23: Rejection of Butanol and Bis-2-Chloroethyl Ether vs effective osmotic pressure in osmotic concentration runs C-37, C-49.

In analyzing the rejection properties of an osmotic concentration system, one must bear in mind that the rejection coefficient in the osmotic concentration process (but not in the RO process) is very much influenced by the presence of the concentrated pump solution. The ability of a solute to permeate from the membrane into the pump solution is highly dependent upon its ability to be dissolved in this solution. At the same time the buildup of salt concentration in the water compartment progressively raises the activity of the organic solute in the water compartment, hence leading to higher values of S. In general, this means that the rejection properties of the system can be modified according to the pump solution compound. This is a subject for further study.

3.3 MEMBRANE REJECTION AND PRESSURE RELATIONSHIPS

The rejection of solutes by membranes is pressure dependent. This was first indicated in equation (5), which predicts an increase in rejection as a result of increased applied pressure. It was shown in section 3.2 that this relationship does not always apply. In addition to the exceptions noted with osmotic concentration (OC) studies, there are data in the literature which illustrate a number of responses different from those that would be predicted by equation (5). Plots (Figures 24-25) of the rejections by cellulose acetate in the reverse osmosis (RO) data tabulated in Table 1, Appendix C, illustrate two distinct and opposite kinds of responses. In one case rejection increases with increasing pressure; in other cases, rejection falls with increasing pressure. It is very difficult to find a simple explanation which will predict what class of compound will respond one way or the other, i.e., which compounds are rejected better at higher pressure, and which at lower pressure.

The deviations from the results predicted by equation (5) indicate that coupled flows between the water and the solute permeating the membrane occur. Extreme coupling occurs when the decrease in rejection is a result of increased pressure. This is a significant factor in concentrating organics by RO or OC because it indicates that care must be exercised in selecting the pressures at which cellulose acetate membranes are to be operated for maximum recovery of contaminant. However, both the NS-1 and the polyamide membranes are much less responsive in this respect. Tables 2 and 4, Appendix C, indicate that for most solutes tested the rejection increases with increasing pressure.

For those solute/membrane combinations which do not obey equation (5), a correction to the equation has been derived from irreversible thermodynamics (25). The modified equation is:

$$R = \sigma \frac{\exp(BJ) - 1}{\exp(BJ) - \sigma} \qquad (10)$$

where $B = (\frac{1 - \sigma}{\bar{p}})$

The term σ is a "reflection" coefficient defined operationally. Its value is generally less than 1.0, and in most instances it is greater than zero. In special cases σ may exhibit negative values. When $\sigma = 1.0$, the equation above reduces to the previous equation (5). When σ is not equal to 1.0, the equation predicts that the rejection will respond to the flux, J; since the flux is proportional to applied pressure, one sees the relationship between rejection and applied pressure. At infinite J (or infinite pressure) $R = \sigma$.

That is,

where $R = \sigma$

then $J \to \infty$

$P \to \infty$

This is a very important relationship because it describes the boundary limit of membrane/solute rejection. For the case where rejection is increased with increased pressure, the σ value will give the ultimate rejection that can be achieved. In the opposite case where rejection increases with decreased pressure it is obvious that operation at low pressure is necessary to achieve maximum rejection.

To use equation (10) above, one needs to have values for J, and for the solute permeability coefficient $\bar{p}$. Then an iteration of trial values of σ to yield measured values of R can be undertaken. An alternate method of computing σ, for subsequent use to predict R at other pressures, is to measure the rejection at two fluxes. Values for σ that satisfy both equations under certain conditions can be found. Once σ is known,

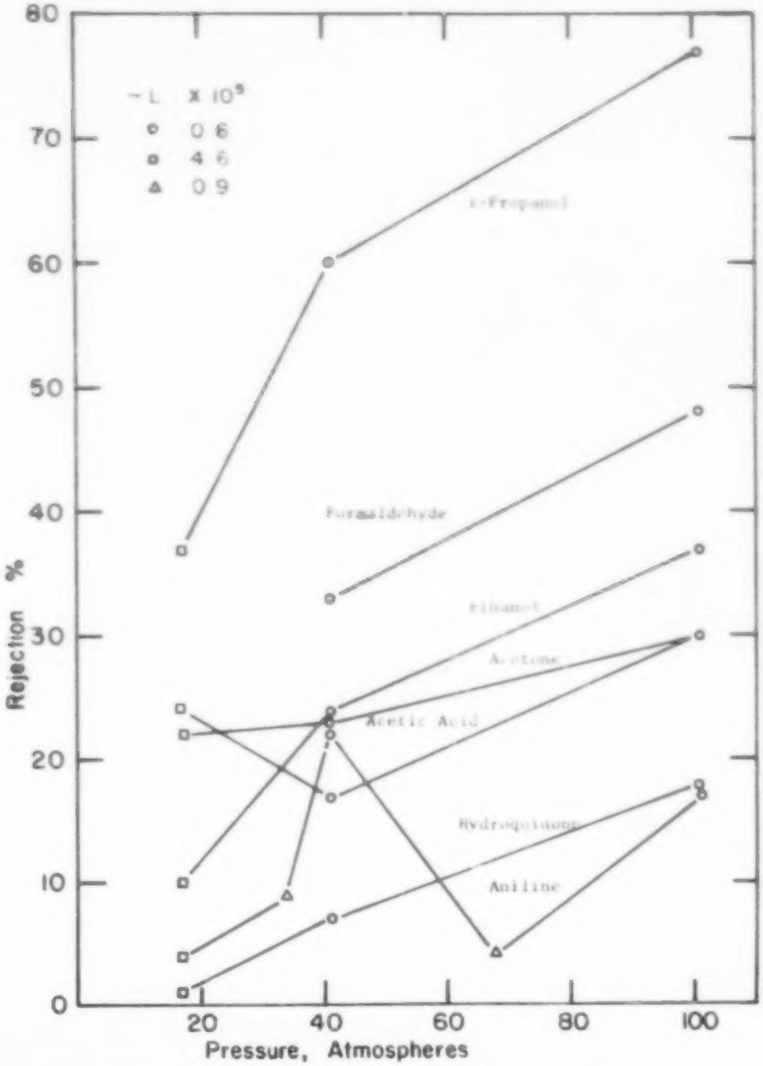

Fig. 24: Rejection increase vs pressure increase of various compounds by cellulose acetate membranes. (Different point notations denote different membranes.)

See Table 1, Appendix C.

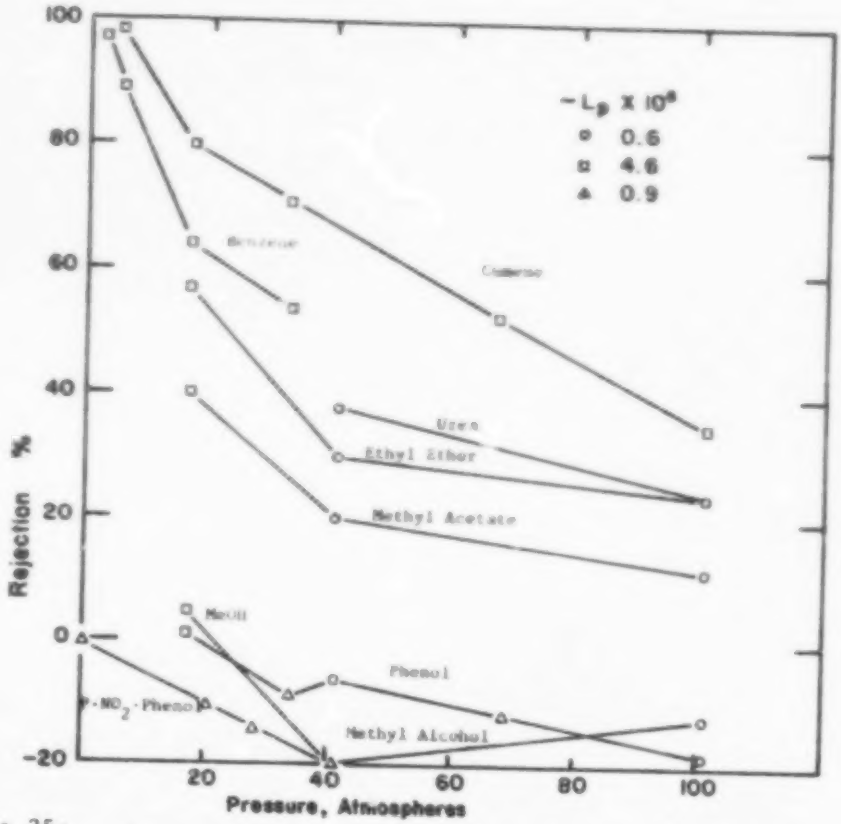

Figure 25: Rejection decrease vs pressure increase of various compounds by cellulose acetate membranes. (Different point notations denote different membranes.)

See Table 1, Appendix C.

the preferred operating pressure can be selected by use of equation (10).

In this study, calculations of σ have been made from data using cellulose acetate and NS-1 membranes for those solutes where the rejection is found to increase with pressure, as illustrated in Figure 24. The results of such calculations are given in Tables 8 and 9. The calculation for p-chlorophenol for the NS-1 membrane yielded a σ value corresponding to the asymptotic value for R (Figure 13), as predicted by equation (10). The calculations for butanol and ethylmethyl ketone were based on the measured value of $\overline{p}$ and one measured value of R.

TABLE 8 Calculated σ for Cellulose Acetate Membrane

$$(Lp = 0.6 \times 10^{-5} \frac{g}{cm^2 \text{ sec atm}})$$

	R_1(40.8 atm)	R_2(102 atm)	σ
Ethanol	.24	.37	.47
Isopropanol	.6	.77	.90
Acetic Acid	.17	.30	.48
Formaldehyde	.33	.48	.57
Acetone	.23	.30	.33
Glycerol	.95	.98	.99

TABLE 9 Calculated σ for NS-1 Membranes

	R_1(40.8 atm)	R_2(102 atm)	σ	$Lp \times 10^5$ $\frac{g}{cm^2 \text{ sec atm}}$
Ethanol	.65	.73	.78	1.1
Phenol	.68	.702	.703	1.1
Formaldehyde	.38	.50	.613	1.3
Acetic Acid	.48	.698	.905	1.3
Hydroquinone	.82	.86	.91	1.1
p-Chlorophenol	.66 (17 atm)	.79 (40.8 atm)	.803	1.0
Butanol	.942(54.4atm)	--	.9999	1.0
Methylethylketone	.908(54.4atm)	--	.91	1.0

1.4 SOLUTE AND MEMBRANE REJECTION RELATIONSHIPS

In the preceding sections tabulated data have been presented for the response of several membranes to a variety of solutes. These data can be correlated by functional group types in the case of cellulose acetate, as shown in Figure 8. However, it is desirable to be able to project the interaction between any membrane material and any solute. To this end, a more general analytical approach than that reported by Matsuura and Sourirajan (16-21) must be taken. If it is possible to construct a general relationship between membrane and solute behavior based on inherent state properties, then the selection of membranes can be simplified by a knowledge of such properties. Alternatively, one could project the probability of rejection of certain solutes by a given membrane. Such information would allow selection of series treatments which would have high recovery efficiencies when used to concentrate organics from water sources.

In an earlier section of this report it was shown that the rejection by a membrane of a series of solutes is a function of the solute type; this was evidenced especially by the response of cellulose acetate. The response is related to the interaction between the membrane and the solute. Those membranes that have high affinities for the solute, exhibit low rejections; those membranes that have low solute interactions, exhibit high rejections. On this basis it is rational that a descriptive system which reflects the degree of interaction between any solute and the membrane would be useful in predicting rejections. Such a scheme has been developed by Hansen using the Hildebrand solubility parameters of organic compounds (14). The solubility parameter δ is a measure of the square root of the "cohesive energy density" of a pure compound. Thus it is a projection of all the molecular interaction of the pure compound.

Hansen elaborated the Hildebrand solubility parameter concept by dividing the parameter into three components: δ_d which reflects London forces, δ_p which reflects polar interactions, and δ_h which reflects the hydrogen bonding interactions. The plane (or space) which is defined by the use of either two or three coordinates serves as a locus for every organic compound. That is, each compound can be defined by either a two- or three-dimensional coordinate given by its particular solubility parameter values. Similarly, every polymer can be defined by an area (or volume in the space) in such a coordinate system, bounded by the coordinates for all those compounds which serve as a solvent for the polymer. In such a coordinate system the differences in chemical affinities between organic molecules and a polymer are indicated by the differences in the vector distances from the center of the polymer's solubility space to the coordinates of the compounds. Organic compounds whose coordinates are not within the boundaries of a polymer's solubility area are not solvents for the polymer. Generally, the closer the solute coordinates come to the boundaries of this area, the greater will be the interaction between the polymer and the solute. Thus as the coordinates of a solute come closer to the polymer boundary, the polymer becomes a better solvent for the solute.

As a practical matter, Hansen found that for most polymer-solute systems a two-dimensional representation using δ_h and δ_p was adequate to describe solvent effects.

Such an approach to predicting mutual miscibility neglects the solubility attributable to the free volume in the polymeric membrane, which will rank solubility in the membrane according to solute shape and dimensions. It places emphasis on the interaction due to specific bonding forces. While the approach to polymer-solute miscibility is contingent on all of the assumptions inherent in the Hildebrand formulation of the problem, it allows an estimate of solubility based on broad molecular properties.

Using these solubility parameters, one can screen a large number of solutes representing examples having a diversity of functional groups, and examine the effect of such groups on the observed solubility in the polymer.

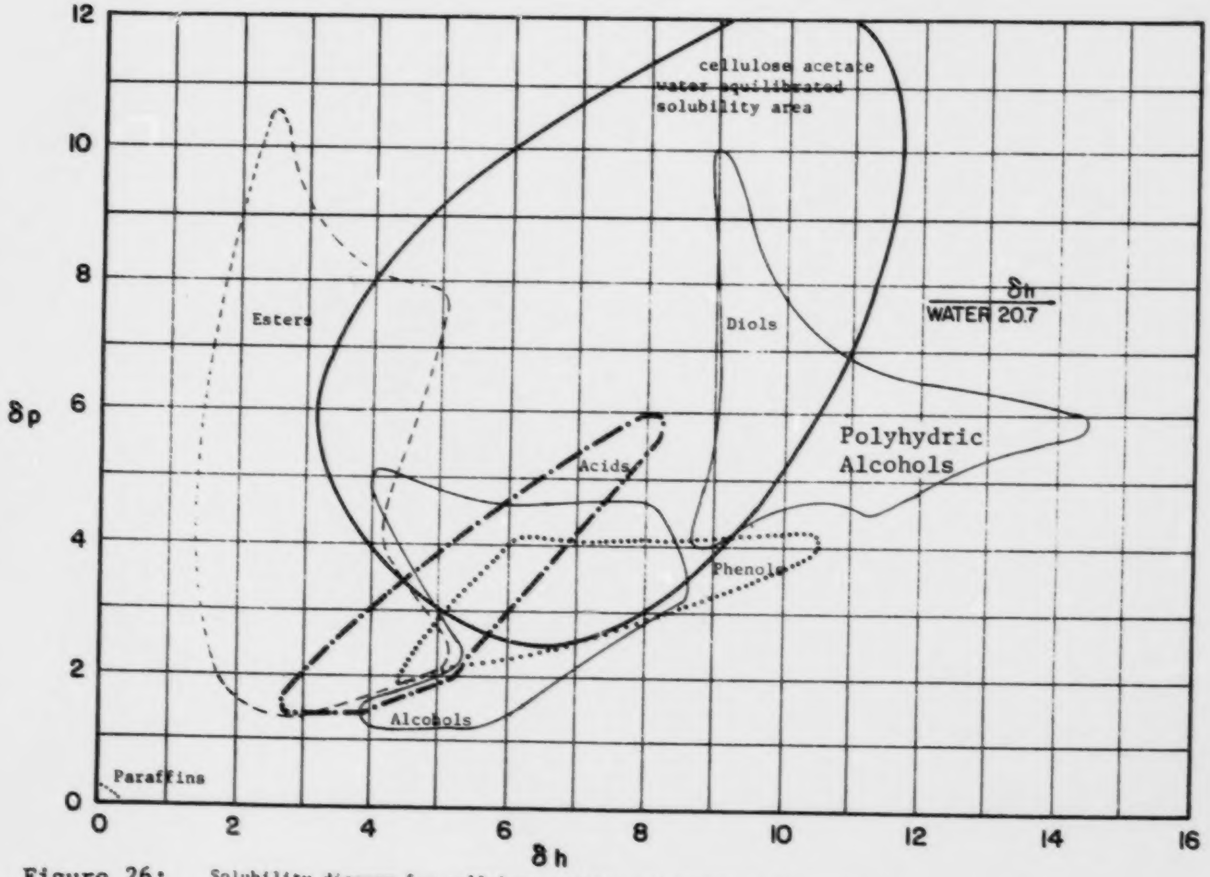

Figure 26: Solubility diagram for cellulose acetate and various solute classes.

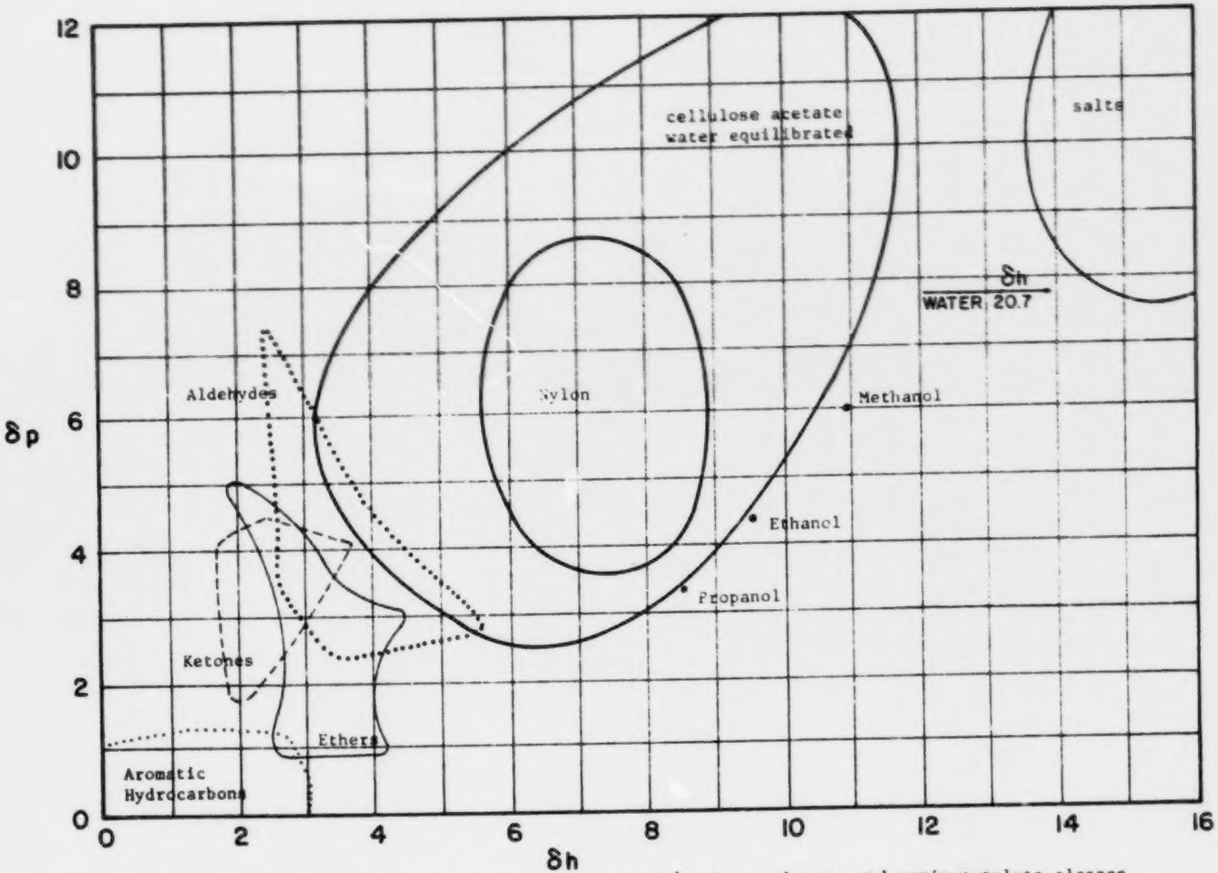

Figure 27: Solubility diagram for cellulose acetate and nylon membranes and various solute classes.

Examination of the spectrum of compounds which are well rejected, and those which are poorly rejected, shows empirically that those solutes whose solubility parameters lie far from those of cellulose acetate are in fact rejected, while those whose parameters lie close to the cellulose acetate area are poorly rejected. One can speculate that this is a direct reflection of the interaction between the pure solute and the polymer from which the membrane is prepared.

However, such a view oversimplifies the actual situation prevailing during the osmotic experiment. The solute is not present in the pure state, but as a dilute solute in water; similarly, the polymer is not the pure polymer, but has dissolved in it several percent of water. Thus one must examine the relationship of a hydrated solute to a polymer in which water is dissolved. Nevertheless, as a simple guide, it is found that the location of the solute with respect to the membrane in this representation is quite a useful predictor. Figures 26 and 27 show the solubility parameter for cellulose acetate equilibrated with water. Compound groups are identified by the area in which they are generally located. From this figure one can predict high rejection of salts, paraffins, cyclic paraffins, and aromatic hydrocarbons by the cellulose acetate membrane. Aldehydes, esters, and diols which have moderate rejections are found near the boundaries of the membrane area. Phenols, carboxylic acids, and alcohols, which are in the solubility area, have low rejections. However, some compounds such as methanol which are found outside the area still have been found to have high permeabilities.

Thus one can use this guide empirically with some measure of success. In Part II of this report, a more theoretical analysis of the interaction problem will be presented, together with some evidence that loss of rejection may be due to interaction between the solute and the membrane water.

As described earlier in this report, the observed rejection is a function of the water flux and the permeability rate of solute through the membrane;

and these two variables can determine the reflection coefficient σ. The σ value is a measure of the relative competitive interaction between solute and membrane, compared to the solute-water interaction in the membrane. If $\sigma << 1$, then a relatively strong affinity between the water in the membrane and the solute, in comparison to the solute-membrane interaction, is predicted. If there is a strong interaction between solute and membrane compared to the solute-water interaction, the σ value will approach 1.0. Thus the σ value is probably the factor which is best predicted by the solubility parameter concept; this in turn leads to the general predictive scheme, since the σ value is a factor in the rejection equation (10). A mathematical treatment of this is given in Part II.

An examination of the rejection of alkyl alcohols by cellulose acetate may serve to illustrate this concept. Methanol, the first in the alcohol series, has a negative rejection*; its solubility parameter is in the far right corner of Figure 27, approaching that of water. Ethanol, whose parameters are toward the left of methanol, closer to the membrane area, is rejected to about 37%; isopropanol, closer yet to the membrane is rejected to 77%. All three alcohols are outside of the boundary of the membrane area. Thus all three would be predicted to show relatively poor interaction with the membrane, and strong interaction with water. Calculation of the σ values yields a negative value for MeOH, 0.47 for EtOH, and 0.90 for i-PrOH. These numbers reflect a decreasing interaction with water as the series increases. Thus although the simple interaction concept based on the membrane-solute couple alone would predict a different order of rejection, the relative interaction between membrane-solute and water-solute is reflected by the σ value. The solubility parameter concept can be used to predict competitive effects between the three components: the membrane, the solvent (water), and the solute, as discussed in Part II.

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* Pressure 102 atm; $L_p = 0.6$; see Table 1, Appendix C.

PART II

4.0 THEORY OF SOLUTE TRANSPORT MECHANISM

Historically, the separation process has been approached from the basis of a porous model of the membrane. According to this model it is assumed that all flow occurs through pores having a characteristic size distribution, which comprise a certain fraction of the membrane. Flow rate and selectivity are governed by pore size distribution and by specific interaction within the fluid in the pores. Sourirajan and coworkers (26) use this model to explain the separation of solutes by the cellulose acetate membrane. However, closer study increasingly indicated that water does not pass by viscous flow through the pores but is dissolved in the dense cellulose acetate layer. The extremely low salt permeability (compared to high permeability of rather large organic molecules like the diacids) and the nearly independent flows of salt and water are difficult to explain by the porous model. The diffusion of labeled water through the cellulose acetate membrane and the water permeability derived from flow under pressure are much less than would be expected for a pore flow (27). So, although this model has an obvious conceptual attractiveness, the authors of the present study believe that the main transport phenomena through the membrane occur by a diffusion mechanism.

The permeation behavior of solute and solvent through the membrane can be treated in terms of uncoupled flow models in which the flux of both water and solute obey Fick's law:

$$J_i = -D_i \, dC_i/dx \qquad (11)$$

where J_i = the flux of component i

C_i = the concentration of component i in the membrane

D_i = the diffusion coefficient (within the membrane) of component i

x = the thickness of the diffusion path

Equation (11) can be restated for water in terms of measurable quantities (see reference 28).

$$J_w = \frac{-D\ C\ V}{RT\ \Delta x}\ (\Delta P_h - \Delta\pi) \qquad (12)$$

$$= -L_p\,(\Delta P_h - \Delta\pi)$$

where J_w = the water flux (cm^3/min)

V = the partial molar volume of water

RT = the gas constant temperature product

$\Delta P = P_1 - P_2$, the resultant hydraulic pressure

$\Delta\pi$ = effective osmotic pressure

C = 55.5 M (water molar concentration)

The solute flux expression can be derived from equation (11) to yield:

$$J_s = D_s \frac{d\bar{c}}{dx}$$

$$= \frac{D_s S\ (C_f - C_p)}{x}$$

$$= \bar{P}\ (C_f - C_p) \qquad (3)$$

where

J_s = solute flux (g $cm^{-2} sec^{-1}$)

D_s = solute diffusion coefficient in the membrane (cm^2/sec,

$d\bar{c}/dx$ = solute gradient in the membrane

S = distribution coefficient between solution and membrane from equation (6)

C_f = solute concentration in feed

C_p = solute concentration in product solution

$\bar{p}$ = the "practical" permeability coefficient of solute and equals DS/x

In membrane permeability studies the product p = DS is frequently used as the permeability coefficient. While it is difficult to determine the value of p, the permeability, from simple experiments, it is relatively simple to determine $\bar{p}$, the permeability coefficient. The difficulty of determination of p results from the asymmetric nature of membranes used in these processes. In such membranes the true thickness of the rejecting layer is not known and x must be estimated.

Equation (3) has been found to be a good approximation for the flux of salts in experiments using reverse osmosis, even though a more nearly correct expression of the equation would be based on chemical potential instead of concentrations.

The magnitude of rejection is obtained from the relationship:

$$R = 1 - C_p/C_f \qquad (4)$$

If no coupling occurs, the product concentration is determined by the relative flows of the solute and the water:

$$C_p = J_s/J_w \qquad (13)$$

which on substitution of equations (12) and (3) yields:

$$C_p = \frac{(C_f - C_p)\ \bar{p}}{L_p \Delta P}$$

which on rearrangement and substitution for C_f leads to

$$R = \frac{L_p \Delta P}{L_p \Delta P + \bar{p}} \qquad (5)$$

Equation (5) is the rejection equation for the membrane-water-solute system, assuming that no coupling occurs between the solute and water. As the water flux increases with increasing ΔP, R approaches its maximum value and the result is increased rejection. In the ideal case where $L_p \Delta P >> \bar{p}$, R approaches 1.0.

Experimentally determined rejections, R, of organic solutes often deviate from the rejections calculated from equation (5) using the permeability coefficient. This phenomenon was found to be characteristic of the transport in biological membrane systems, in which the flow of each component is in many cases additionally determined by the flows of other components; that is, the flows are coupled. This type of behavior can be predicted from irreversible thermodynamics. Kedem and Katchalsky (29) derived a set of equations which are comparable to equations (12) and (3) but which are more general.

$$J_v = L_p \, (\Delta P_h - \sigma \Delta \pi) \qquad (14)$$

$$J_s = -p \frac{dC_s}{dx} + (1-\sigma) \, C_s J_v \qquad (15)$$

where J_v = the volume flux, which is nearly identical to water flux

ΔP_h = the resultant hydraulic pressure

$\Delta \pi$ = the resultant osmotic pressure

$(\Delta P_h - \sigma \Delta \pi)$ = ΔP, the resultant total pressure that is used in equation (5)

σ = the reflection coefficient, which in this study is a measure of water solute flow coupling within the membrane

$\bar{p}$ = the local permeability coefficient, which equals DS.

In the case that $\sigma = 1$, there is no flow coupling within the membrane. When $\sigma < 1$, the flows are coupled. Based on equations (14) and (15), the solute rejection in terms of pressure and permeability is given by

$$R = \sigma \frac{1 - \exp\left[-L_p(\Delta P_h - \sigma\Delta\pi)(1 - \sigma)/\bar{p}\right]}{1 - \sigma\exp\left[-L_p(\Delta P_h - \sigma\Delta\pi)(1 - \sigma)/\bar{p}\right]} \tag{16}$$

or in terms of volume flow:

$$R = \sigma \frac{1 - \exp[-J_v(1-\sigma)/\bar{p}]}{1 - \sigma\exp[-J_v(1 - \sigma)/\bar{p}]} \tag{17}$$

At the high pressure limits $J_v \rightarrow \infty$ and $R \rightarrow \sigma$. As σ approaches unity, equation (16) reduces to equation (5).

There are no conflicts between the diffusion model theory and the irreversible thermodynamic treatment that is projected in equations (16) and (17). However, the difference in the σ values of two different membranes toward a certain solute may reflect differences in the separation mechanisms of these two membranes.

With these definitions, one can classify the observed transport in terms of the properties of the membrane, the solute, and the interactions between these two and the water. As a starting point one must bear in mind that the permeability through a diffusion governed membrane is given by:

$$p = D\ S \tag{18}$$

On the basis of this relationship one should be able to measure p and S independently, and from the product classify the various solutes in terms of their expected behavior. Such classifications could then be compared to experimental observations of the solute separation.

The solubility S of a solute is the result of the balance of forces between (i) the membrane phase and the solute; and (ii) the water and solute in the solution. Note that the membrane phase is a water-swollen polymer.

The thermodynamic parameters which describe the solubility S are the chemical potentials μ of the solute in each phase. For any transport to occur, it is apparent that S must be greater than 0, since otherwise no gradient would be established in the membrane. The value of S will increase if the chemical potential of the solute in water (μ_{sw}) increases faster than the chemical potential of the solute in the membrane. This is analogous to the "salting out" phenomenon.

For inorganic salts distributed between water and the known reverse osmosis membranes, $\mu_{sm} >> \mu_{sw}$, and S is very low. This is true both for those salts present in the associated form, and for those in the dissociated form. For dissociated ions, the work required to bring a charged species into a volume of low dielectric is very great. Consequently, the solubility of highly charged ions in the membrane is extremely low.

Analyses of the permeability results with a number of organic solutes allows arbitrary grouping of solutes into three general classes:

Class I: $0 < S \leq 1$
Class II: $1 \leq S < 10$
Class III: $10 \leq S$

The Class I solutes are those species which have a low chemical potential in water relative to their chemical potential in the membrane. This may be the result of high molecular weight or molecular shape factors which physically prevent the solutes from penetrating the dense polymer network. Or it may result from strong interactions between water and the solute, compared to the solute-membrane interaction. These strong water-solute interactions may in some cases lead to the formation of hydrated solute molecules whose dimensions are greater than can be accommodated by the polymer network.

The Class II compounds represent the large number of organics which in their pure state would be considered swelling agents or solvents for the water-swollen polymer, and which have sufficient interaction with water to form hydrates. Thus furaldehyde, butanol, and acrylamide would swell the polymer in their pure form, and in aqueous solution form hydrates.

Class III compounds are those exhibiting anomalous distribution coefficients, either because of specific interactions, such as surface absorption phenomena (phenols), or because they have high chemical potentials in water. For the latter case, the properties of the medium are the dominating factor, rather than the specific interaction. For example, xylene has no specific interaction with either water or the polymer, but the membrane medium is a "better solvent" than the water (i.e., $\mu_{sm} < \mu_{sw}$), and S is found to be relatively quite high (Table 10).
Attempts to correlate these three observed categories with the solubility parameter concept of Hansen (14) have met with considerable difficulty. Because the interaction must be applicable to a three-component system, some of the categories describe energies of mixing which are not amenable to the simple solubility parameter constraints. For example, if purely additive rules of enthalpy of mixing were to apply, one could expect to compare the vector distance on the Hansen diagram between the center of polymer solubility and the solute coordinates, given by:

$$1^{sp} = [(\delta^{s} - \delta^{p})_{p}^{2} + (\delta^{s} - \delta^{p})_{h}^{2}]^{\frac{1}{2}}$$

(where superscripts s and p refer to solute and polymer coordinates) to the distance between the solute coordinate and the water coordinate, given by

$$1^{sw} = [(\delta^s - \delta^w)_p^2 + (\delta^s - \delta^w)_h^2]^{\frac{1}{2}}$$

and decide on this basis what the distribution coefficient will be. However, the additivity is not linear because of non-enthalpic contributions to the energy of mixing.

An empirical correlation for cellulose acetate which is applicable to a large number of solutes has been found. In Figure 28 the dashed ellipse represents the solubility area of cellulose acetate. In the present application the cellulose polymer contains 13.5% w/w water; consequently its corrected solubility area is shifted toward the water coordinates ($\delta_p = 7.8$, $\delta_h = 20.7$, from reference 14). A solubility parameter vector (or solubility parameter radius) is defined as $1^{o,i} = (\delta_p^2 + \delta_h^2)_i^{\frac{1}{2}}$. The area swept by this vector as it rotates about the origin will include the coordinates of all compounds having an equal or smaller vector distance from the origin. When the distances from the origin for several compounds are plotted versus the distribution coefficient, the relationship shown in Figure 29 is derived. There is a linear decrease in distribution coefficient up to the solubility vector values corresponding to butanol; after that point this relationship no longer holds.

The compounds which obey the relationship are those which have only limited interaction with either the membrane or the water. Solutes which form hydrates or which have specific interactions (e.g., phenol) do not obey the relationship, probably because the chemical potential terms which must be used differ significantly from the enthalpy terms incorporated into the solubility parameter concept.

Other correlations using the solubility parameters and a variety of interpretations of correlations between solubility parameter functions and the distribution coefficient S are currently under study in this laboratory. See for example Appendix B.

The diffusion coefficient is governed by two separate interactions: (i) solute polymeric matrix interaction, designated f_{sm}; and (ii) solute water interaction, designated f_{sw}. The f's have been considered frictional coefficients by some authors (25), although such an analytical designation is not necessary, since any interactive force would lead to the same result. The terms f_{sm} and f_{sw} can also be viewed as a measure of the solute's interaction with the static (polymer) and mobile (water) components in the membrane, respectively.

As in the case of solubility S one can classify the various diffusive transports for different solutes. Thus the diffusion coefficients for electrolytes in cellulose acetate membranes are found to be quite low. This is true both for associated and dissociated electrolytes (7). It is important to remember that in the membrane the major mobile species is water. Thus any solute in the hydrated membrane which interacts strongly with water will have increased diffusivity due to this interaction. The phenomenon is termed "coupling". Thus ionized salts which are hydrated would be expected to show increased diffusivities, but in fact do not. The low diffusivities which are found must result from electroneutrality balance requirements. Undissociated salts which are not hydrated behave as organic solutes.

The diffusivities of pure species present in a polymer below its glass transition temperature, at concentrations approaching 0, are all generally less than 10^{-9} cm^2/sec (6,30). (Concentrations approaching 0 resemble the solute concentrations discussed in this study.) Thus for acetone, which is a good solvent for cellulose acetate, the diffusivity at infinite dilution is below 10^{-12} cm^2/sec in this polymer (as calculated from reference 31). However, when the diffusion is measured from a water equilibrated membrane using a low concentration aqueous solution, the diffusivity is $10^{-8}cm^2/sec$ (see Table 10). Since the diffusivity of water in the membrane is approximately $10^{-6}cm^2/sec$, such results indicate that the water is accelerating the mobility (or transport rate) of the acetone. This is in accord with the solubility observations (S) that acetone is distributed preferentially into water.

Another measure of the "coupling" is the σ value determined from equation (16). For acetone a σ value of 0.33 (Table 10) indicates significant interaction between the acetone and the water in the membrane phase.

The diffusion coefficients D of the organic solutes and the distribution coefficients S show a correlation which is in agreement with the arguments of the discussion above. Figure 30 shows that those species which show a strong water interaction -- and therefore a low distribution coefficient into the membrane -- also show a high diffusivity. Conversely, those compounds which exhibit lower water affinities, reflected in higher distribution coefficients, also show low diffusivities. The relationship appears to follow a power law, as shown by its linearity. The striking result from this relationship is that all of the permeabilities p are reduced to values in the range of $10^{-8}cm^2/sec$, although the diffusivities vary from $10^{-7}cm^2/sec$ to $10^{-10}cm^2/sec$.

To use the relationships outlined for p to calculate rejection, one must still search for a predictive method for estimating σ. The derivation of σ in terms of frictional coefficients has been studied by Spiegler and Kedem (32), and is given in equation (19)

$$\sigma = 1 - K \left(\frac{f_{sw}}{f_{sw} + f_{sm}} \right) \qquad (19)$$

where K = S/volume of water in the membrane

The friction coefficient in equation (19), when translated in terms of chemical interactions in the solute-polymer-water system, can be related to some proportionality of the difference of the solubility parameter of each couple, solute-water, solute-polymer. This would lead to a uniform method of prediction of the rejection, or "coupling," in terms of the reflection coefficient σ. A method to calculate the distribution coefficient S in a water-solute-membrane system, when the solubility of the organic solute in water is known, was developed in this study in cooperation with Dr. David Bonner (see Appendix B). Since S and D are inversely related, all of the parameters of equation (19) relating volume flux, rejection, and permeability will be subject to estimation.

In Part I it was demonstrated that two opposite responses to an increase in applied pressure are found: for some solutes increased rejection is found with increased pressure; for others decreased rejection is observed. In the case of increased rejection the σ value is positive and can be calculated from equation (16). A decrease in rejection may lead to a negative σ, which means enrichment of the product. Such a case cannot be explained by the simple diffusional model used in this study. Negative rejection actually means that transport of the solute is against the gradient of the solute in the membrane. It cannot be explained by the coupling effect alone, because the coupling effect might in extreme cases lead to zero rejection (disregarding the case where the permeability of the solute is higher than that of water). A decrease of solute rejection with increased pressure accords with the behavior of Class III solutes (i.e., $S > 10$). High interaction of these solutes in the membrane interface will give rise to a change in the inherent properties of the membrane interface (e.g., plasticization) which will enhance the penetration of solute into the membrane. In the case of phenol it has proved to decrease the water transport (33). High concentration of the solute in the interface, resulting from interaction with the surface of the membrane, will lead to a higher value of μ_{sw} near the surface. The volume fraction of the solute in the interface might be much higher than that in the entire solution, and the effect of the pressure on the solute can no longer be ignored. If the volume is not ignored, equation (5) will take the form:

$$R = \frac{D_w C_w V_w (\Delta P_h - \Delta \pi) - D_s S V_s \Delta P_h}{D_w C_w V_w (\Delta P_h - \Delta \pi) + D_s SRT}$$

and the condition for negative rejection will be:

$$D_s S V_w > D_w C_w V_w$$

However, further studies of membrane interface in this kind of behavior must be made to draw a precise quantitative model.

TABLE 10 DISTRIBUTION AND DIFFUSION COEFFICIENT IN CELLULOSE ACETATE MEMBRANE

	Solutes	S	$D^{a,b} \times 10^{10}$ cm^2/sec	$\bar{p} \times 10^5$ cm/sec	$D^c \times 10^{10}$ cm^2/sec
1.	Phenol	38 (37)[a]	10	16.8	4.5
2.	Acetone	(0.3)[a]	300	-	-
3.	Nitromethane	(2.1)[a]	150	-	-
4.	Pyridine	(0.7)[a]	75	17.3	270
5.	Aniline	(20)[a]	20	15.8	7.9
6.	Dimethylphthalate	18	-	6.27	3.3
7.	Xylene	56	-	7.85	1.4
8.	Ethylene Glycol	5.5	-	-	-
9.	Methyl Ethyl Ketone	1.0	-	18.6	186
10.	Furaldehyde	6	-	20.5	36
11.	Acrylamide	2.5	-	14.3	57
12.	2,4-Dichlorophenol[a]	332	1.5	-	-
13.	2,4 Dichlorophenol[b]	34	5.6	-	-
14.	p-Bromophenol[a]	165	3.8	-	-
15.	Nitrobenzene[a]	54	8.0	-	-
16.	3,5-Di(carbethoxy)phenol[a]	129	1.8	-	-
17.	p-Dichlorobenzene[b]	25	110	-	-

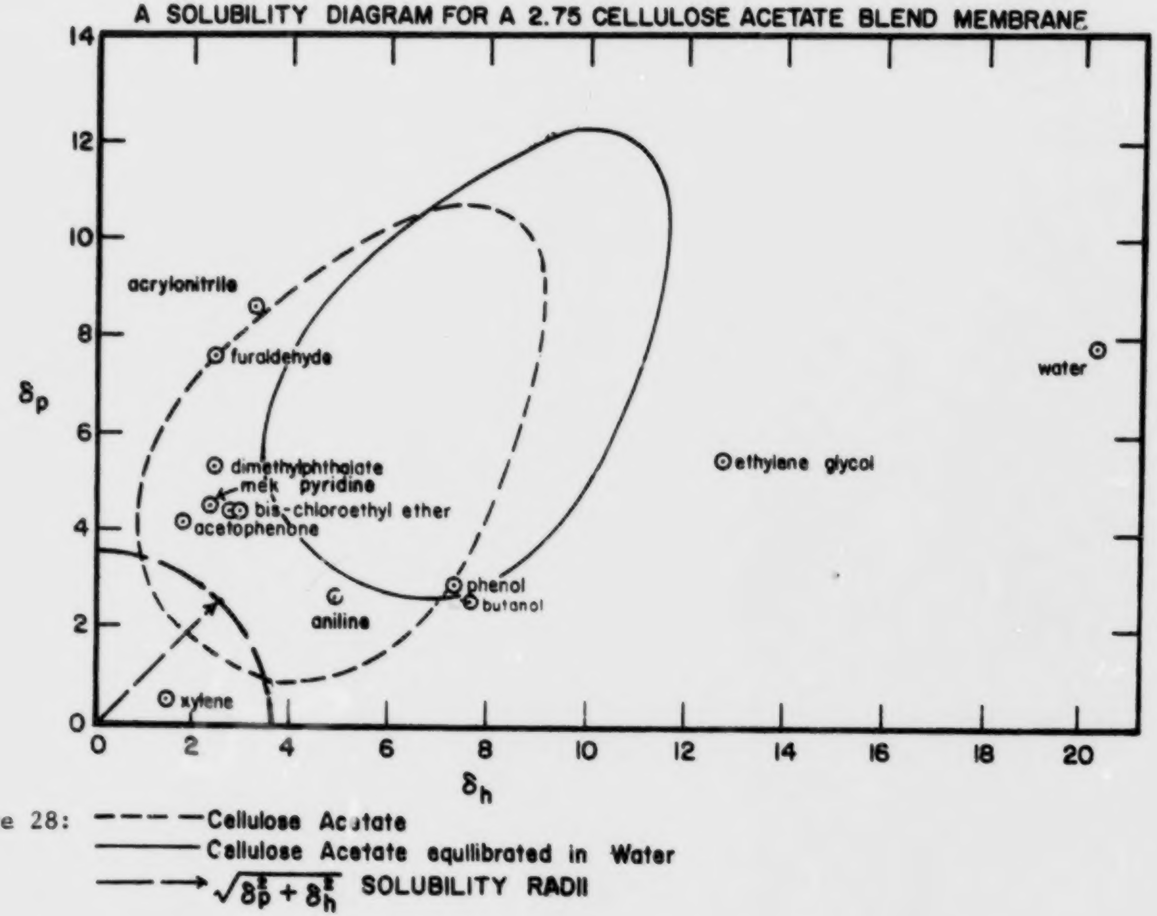
A SOLUBILITY DIAGRAM FOR A 2.75 CELLULOSE ACETATE BLEND MEMBRANE
δ_p
14
12
10
8
6
4
2
0
δ_h
0
2
4
6
8
10
12
14
16
18
20
acrylonitrile
furaldehyde
dimethylphthalate
mek
pyridine
bis-chloroethyl ether
acetophenone
aniline
phenol
butanol
xylene
ethylene glycol
water
Cellulose Acetate
Cellulose Acetate equilibrated in Water
$\sqrt{\delta_p^2 + \delta_h^2}$ SOLUBILITY RADII

Figure 28:

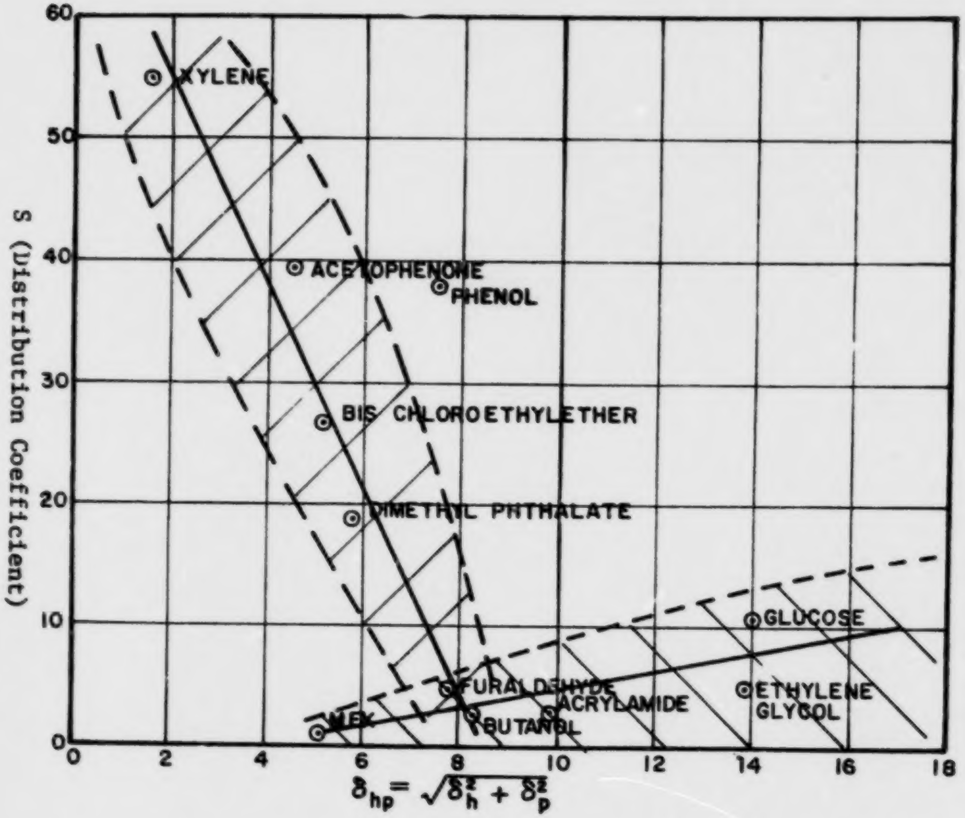

Figure 29: Correlation of the Distribution Coefficient and Solubility Parameter

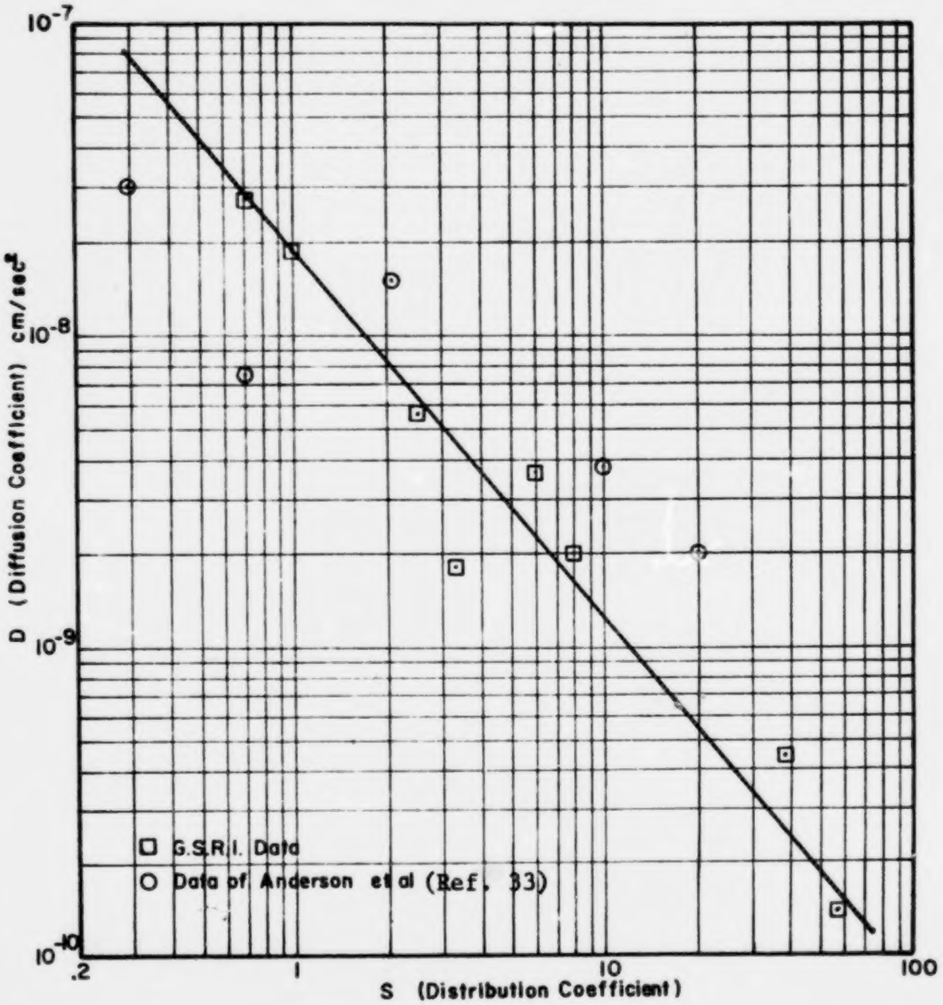

Figure 30: Correlation between the distribution and diffusion coefficients.

GLOSSARY

A = surface area of membrane

B = $\frac{1 - \sigma}{\bar{p}}$

C = concentration

D = diffusion coefficient (cm^2/sec)

f_{sw} = interaction between solute and water

f_{sm} = interaction between solute and membrane

G = weight of transported water

H = Henry's Law constant

J = flux per unit area ($g/cm^2 sec$)

K = S/volume of water in the membrane

L_p = hydraulic permeability constant ($g/cm^2 sec$ atm)

OC = osmotic concentration

OU = osmotic ultrafiltration

P = hydraulic pressure (atm)

ΔP = differential hydraulic pressure (atm)

p = permeability

$\bar{p}$ = permeability coefficient of solute (cm/sec)

ΔQn = amount of solute transported

R = rejection coefficient

RO = reverse osmosis

RT = gas constant temperature product

S = distribution coefficient between solution and membrane (sometimes referred to as solubility)

t = time

V = volume

Wt = weight

x = membrane thickness

Greek Letters

δ = solubility parameter

λ = wave length

μ = chemical potential

π = osmotic pressure (atm)

σ = reflection coefficient

δ_{hp} = $(\delta_p^2 + \delta_h^2)^{\frac{1}{2}}$ = solubility radius

Subscripts

d = dispersion or London forces (used with δ)

eq = equilibrated

f = feed mixture

h = hydrogen bonding (used with δ)

i = initial state or time

1 = final state

m = membrane

o = initial state

p = product solution

p = polar interaction (used with δ)

s = solute

t = time

w = water

1,2 .. solution compartment 1 or 2

Superscripts

a = compartment a

b = compartment b

h = hydrogen bonding

m = membrane

p = polymer

s = solute

t = time

w = water

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APPENDIX A

1.1 OPERATIONAL STUDY OF OSMOTIC ULTRAFILTRATION

Experiments were designed to test several factors that govern the potential utility of osmotic ultrafiltration for concentrating solutes. It was necessary to examine:

a. The performance of an osmotic concentrator in terms of water flux (J_w) as a function of specific pump solute, flow regime through the device, and rejection of pump solutes;

b. The experimental rejection of organic solutes, which can be used to verify the prediction of the transport models being used.

The asymmetric membranes can be used in only one orientation when they are employed in a reverse osmosis unit, viz, with the "dense" skin layer toward the high pressure side. However, in the osmotic concentration mode, the membrane can have its "dense" side facing either the osmotic pump solution, or the water sample side. These two flow configurations are illustrated in Figure 31 and are designated Case I and Case II flow regimes.

When the pump solute is adjacent to the "dense" layer, the product water can be swept away from the surface of the membrane immediately by the rapid flow of pump solution. If mixing is complete, the membrane surface is in equilibrium with a solution corresponding to the average bulk concentration. The organic solutes that were rejected by the membrane "skin" will accumulate temporarily in the membrane pore structure, but will then diffuse back into the bulk water compartment.

When the pump solution is adjacent to the porous side of the membrane, it is displaced from the active layer of the membrane by the thickness of the porous layer. The product water can mix in this regime with the pump solution and thereby dilute the pump ion concentration. The organic solute that is rejected by the dense membrane layer can, however,

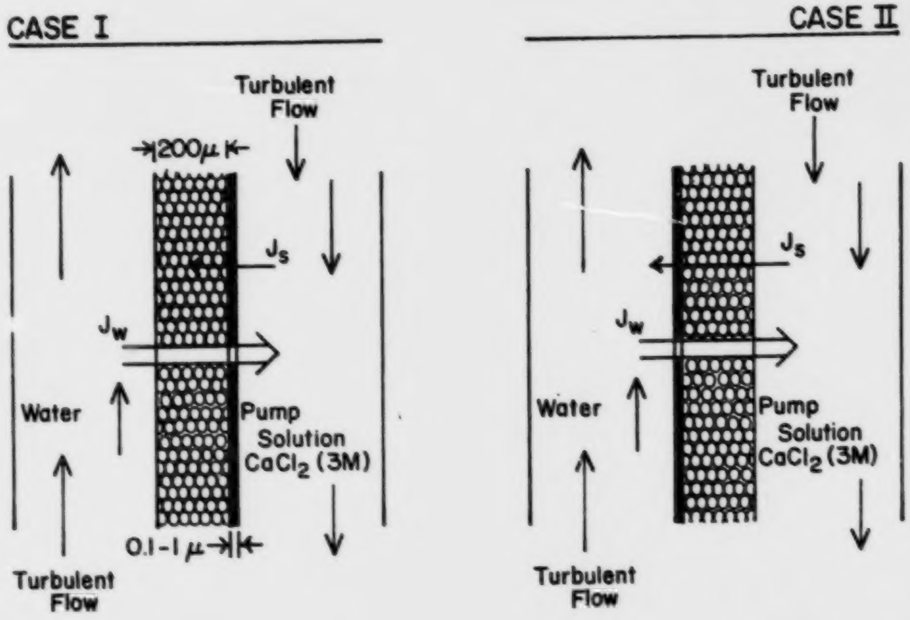
CASE I
CASE II
Turbulent Flow
200μ
J_s
J_w
Water
Pump Solution $CaCl_2$ (3M)
$0.1-1\mu$
Turbulent Flow
Turbulent Flow
J_s
J_w
Water
Pump Solution $CaCl_2$ (3M)
Turbulent Flow

Figure 31: Effect of Membrane Structure on the Osmotic Pressure ($\pi_{eff.}$)

be swept away immediately by the circulation of the water stream.

To determine if these effects are significant, plots of volume transported (V) versus time were constructed from experiments using both the Case I and the Case II flow regimes. From the slope of the V vs time curves, incremental values of the slope can be used to calculate the effective osmotic pressure from equation (2). These osmotic pressure values were then plotted as a function of pump compartment volume (or volume transported) to give a diagram of instantaneous osmotic pressure as a function of concentration. In Figures 32 and 33 these data are shown for both Case I and Case II experiments using a membrane area of 1025 cm^2 and 3.4 molar $CaCl_2$. Over nearly the entire range of concentrations, the osmotic pressure generated in Case II is only about 70% of the osmotic pressure generated in Case I flows, in accord with the possible mechanism outlined earlier. Even the Case I regime provides an effective osmotic pressure of about 100 atm at a solute concentration of 3.4 M $CaCl_2$ when the theoretical osmotic pressure is 500 atm.; thus the observed osmotic pressure is about 20% of the theoretical value.

Similar efficiencies of osmotic pressure generation were observed with saturated $MgSO_4$ solution as the pump fluid; the theoretical osmotic pressure for such a solution is 136 atm., but observed pressures of only 30-39 atm were obtained with a saturated solution operated in the Case II regime.

Such behavior is a direct result of the transfer of pure water into the boundary layer immediately adjacent to the membrane face. The driving force is based on the solute concentration at this membrane-fluid interface, and if the permeating water is not well mixed with the pump solution the effective driving force is reduced. The effectiveness of mixing is a function of the test cell design, the presence of turbulence promoters, the viscosity of the solution, and the rate of water transfer through the membrane.

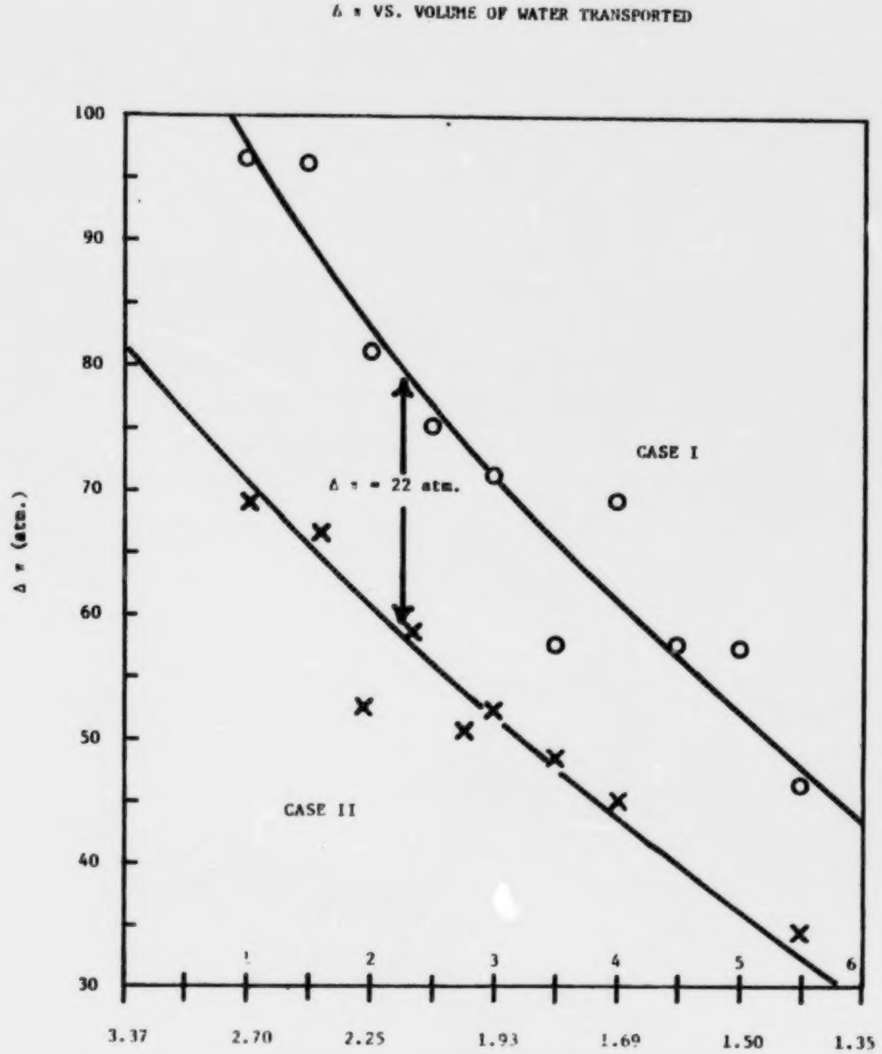

Figure 32: Volume of Transported Water (Lit.) and changes of salt concentration (M) in pump solution respectively.
Initial Volume (6 Lit.)

Changes in transport rate with asymmetric membrane orientation.

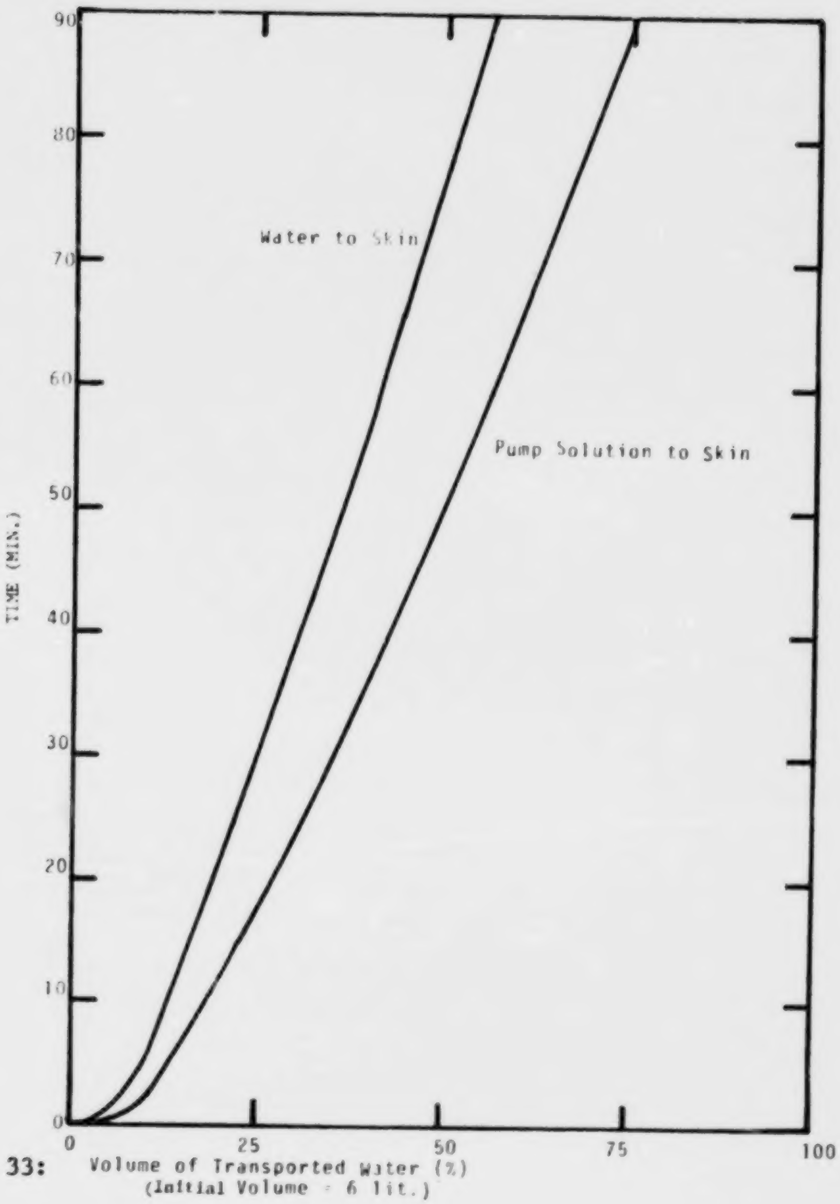

Figure 33:

The effective osmotic pressures cited above indicate that only a portion of the theoretically available driving force is being utilized in the apparatus as presently operated. To determine how much of this loss in efficiency is the result of fluid resistance, a series of experiments was conducted to measure the transfer rate of water across the membrane as a function of fluid velocity in the vicinity of the membrane.

The small 95.7 cm^2 membrane cell was loaded with six membrane sheets, pump solution facing the skin; approximately 2.0 molar $CaCl_2$ was used as the pump fluid. The $CaCl_2$ was selected since it has a lower viscosity than the $MgSO_4$ solution at the same osmotic pressure. The velocity of the fluid flowing past the membrane was increased stepwise, and the water transport rate was measured gravimetrically by timing the interval required to reduce the reservoir weight by 10 g increments. An average of four timed intervals was used.

The data are summarized in Table 11. There is a definite increase in transport rate with increasing fluid velocity, up to the maximum that the present flowmeter arrangement would allow. The increased flow reduces the boundary resistance and thus can be expressed as an increased osmotic pressure. These data suggest that perhaps a 20% improvement can be obtained by just fluid velocity increases. However, modification of the design is indicated in that the highest achieved osmotic pressure of 34 atm is less than 10% of the anticipated theoretical osmotic pressure.

Extrapolation of the flow data by the usual analytical methods for fluid resistances indicates that even at "infinite velocity" the osmotic pressure would still be less than 50 atmospheres. This implies that the usual mechanisms of analyzing fluid resistance may not be apropos to the application at hand, and that it would be advisable to use empirical methods to deduce how to achieve the maximum pumping rate with the least contamination of the sample solution.

TABLE 11

Osmotic transfer of water through asymmetric cellulose acetate membrane as a function of the $CaCl_2$ 2 M solution (pump fluid) velocity.

No.	Pump Fluid Flow Rate g/min	Membrane Flux cc/sec	$\Delta\pi$ eff atm.
1	69.8	.172	28.7
2	237	.176	29.3
3	420	.185	30.8
4	622	.197	32.8
5	805	.207	34.5
6	1,003	.205	34.2

The effect of the flow regime on the selectivity of the membrane was studied. The fact that Case II exhibits higher osmotic pressure than Case I should influence the total weight of salt that is to be found in the water compartment because the salt has a different permeation time in the two cases. Moreover since the flux vector of water through the membrane is opposite to the salt flux, any coupling effect (interaction) between the water molecules and the ions should impede the salt permeation more in Case I than in Case II. However, in the experimental result, we find only a slight indication of improved rejection of Case I over Case II, as seen from Figure 34.

In Case I the pump ion concentration at the surface may approach the bulk value, if perfect mixing were to occur. In Case II, where fresh pump ion must arrive at the active layer by diffusion through the porous membrane layer, the concentration will be much lower (as evidenced by the reduced osmotic pressure). But the salt and water fluxes operate in opposite directions, so that reduced water flux coupled with lower ion concentration gradient may result in the same leakage rate as a higher water flux accompanied by a larger ion concentration gradient.

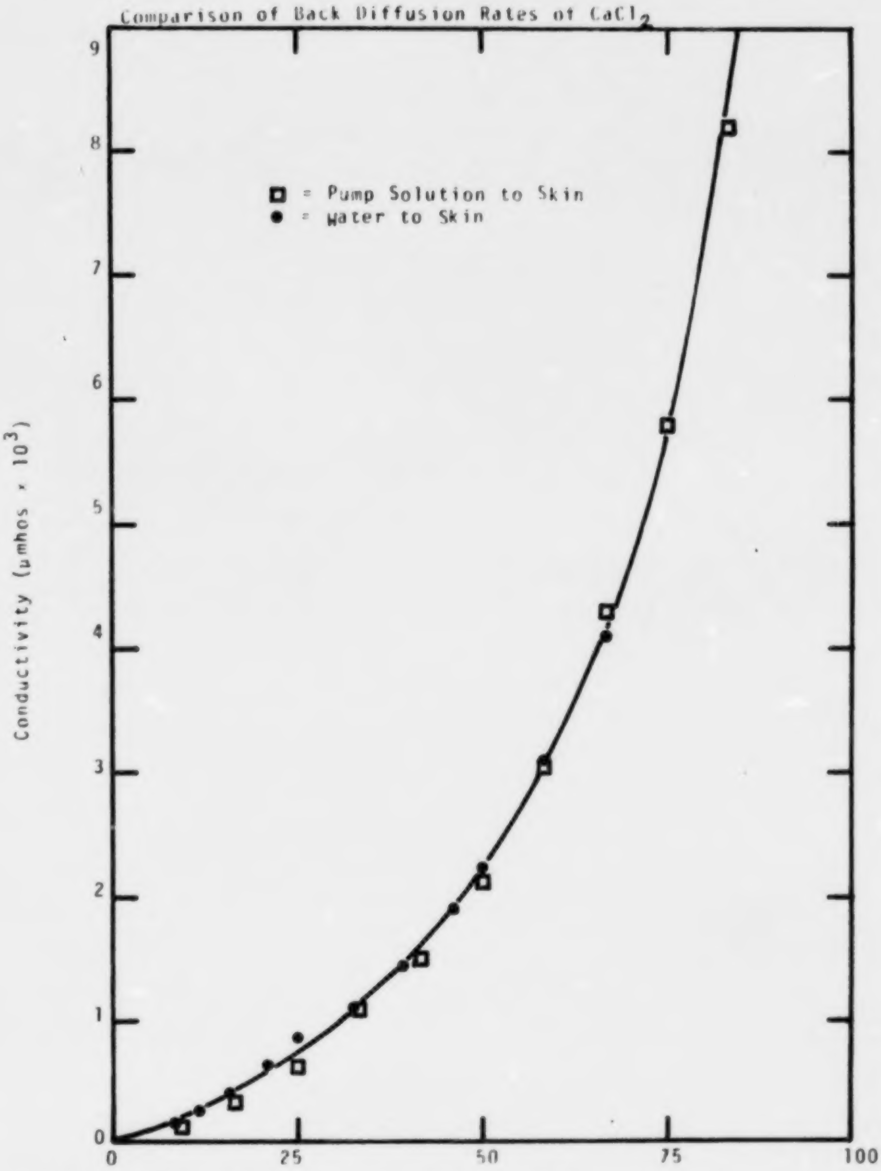

Figure 34: Volume of Transported Water (%)
(Initial Volume 6 lit.)

These balances of effects were in fact observed, as shown in Figure There is virtually no difference in the loss of pump solution whether the system is operated with the pump solution adjacent to the skin side of the membrane, or on the porous side. The conclusion from these studies is that operation in the Case I mode will allow more rapid pumping, but will have no effect on the organic solute contaminant which is to be collected for toxicological studies. As a matter of safety, most of the experiments were performed in the Case II flow regime, to assure that the best rejection possible would be obtained for the solutes, even though this meant slower pumping rates of water. The exact relationships between flow regime and rejection may differ with the intrinsic level of rejection; this will have to be tested in future work.

From the practical aspect, the accumulation of pump solute in the water compartment is undesirable. The flux of the pump solute, i.e. $CaCl_2$, will occur because of imperfections of the membrane. Two types of imperfections may occur:

a. Pores or pinholes in the membrane, usually resulting from damage to the membrane.
b. Poor salt rejection by some of the domains in the membrane.

The first type of imperfection almost always leads to reduced rejection and increased hydraulic flux. The second imperfection is normally manifested by a reduction in the rejection with only incremental increases in flux.

Frequently the first and to a lesser degree the second type of imperfection can be overcome by adding a high molecular weight solute to the feed solution. We have found, for example, that Blue Dextran, 2 million molecular weight, is effective in restoring the rejection of cellulose acetate membranes which appear to have developed pinholes or pores during loading and operation. This solute is not able to penetrate the imperfections and thus plugs the leak. For example, a run which gave us

800 ppm salts in product water, compared to 400 ppm entering the compartment, was reduced to 420 ppm after addition of a very small amount of Blue Dextran. Other high molecular weight plugging agents can be used. Sometimes water solutions which are to be concentrated have enough high molecular weight residue in them to serve as self-plugging agents.

If the imperfections are inherent in the membrane as supplied, this approach of employing plugging agents will probably not be effective. In actual operation any membrane that continues to exhibit high salt leakage rates should be discarded. One must remember, however, that 100% rejection is never achieved and that some $CaCl_2$ or pump solute will always penetrate into the water compartment.

1.2 DONNAN-SOFTENING DEVICE

To avoid severe increases of the inorganics in the water system, as the feed water containing inorganic is concentrated, we have developed a "Donnan-softening" device (Figure 5). The water which discharges from the concentrating cell flows into a loop which contains a cation and anion cell connected in series. The first cell contains an anionic charged membrane to separate the test solution from an inorganic acid such as H_2SO_4 or H_3PO_4. The second cell contains a cationic membrane, separating the solutions from a NaOH solution. Thus a Donnan exchange is carried out between the acid/base solutions and the inorganic salt solutions.

In the first cell Ca^{++} and other cations are exchanged for H^+ and in the second cell Cl^- and other anions are exchanged for OH^-. The net exchange removes inorganic ions and replaces then with water. This process can reduce the amount of inorganics in the concentrate and thus prevent precipitation of inorganics. Its effectiveness is dependent upon the properties of the ion-exchange membrane, i.e., charge density, area, and thickness. Increasing density and area, and decreasing thickness, will increase the rate of this transfer. Table 12 and Figure 35 present the data which were taken from our measurements. From these data it is obvious that the amount of exchange is highly dependent upon the rate of water flow in the loop.

In Table 12 we see from the pH column that the anion exchange membrane cell is much more effective than is the cationic cell. In this case the pH was adjusted to pH 7-8 by reducing the amount (area) of membrane in the anionic cell. The decrease in conductivity shows that there is no leakage of NaOH or H_2SO_4 in either cell, and that there is a progressive decrease in the amount of salt as the salt is replaced by water in the exchange loop.

A high efficiency Donnan-softening device requires high charge density membranes which are thin enough to allow rapid transport of ions from the water cell. Such membranes are under study and development and should be available in the near future.

TABLE 12 DONNAN EXCHANGE OF $CaCl_2$ BY IONIC CELLS WHICH CONTAIN 0.76 N H_2SO_4 and 0.395 N NaOH

	PH			($CaCl_2$) (ppm)			Flow Rate (ml/min)			Conductivity (mho)	
Run	F*	R*	A*	F	R	A	F	R	Acid Circulation	F	R
I	7.15	8.9	2.4	1,425	1,291	1,291	89.5	86	400	2,900	2,700
II	7.15	8.3	2.45	1,425	1,295	1,295	89.5	87.5	45	2,900	2,780
III	7.15	10.08	2.0	1,425	1,071	1,070	20	19.5	19.1	2,900	2,320
IV	7.15	11.5	1.9	1,425	564	563	5-10	5-10	19.1	2,900	420

F* = Feed (Initial solution which was introduced to the ionic cells).

R* = Raffinate (Final product after circulation in the acidic and basic cells respectively).

A* = Product coming from the acidic cell.

Total area of membrane inside each cell was 478 cm^2. Ion exchange membranes are 1/32 inch thick.

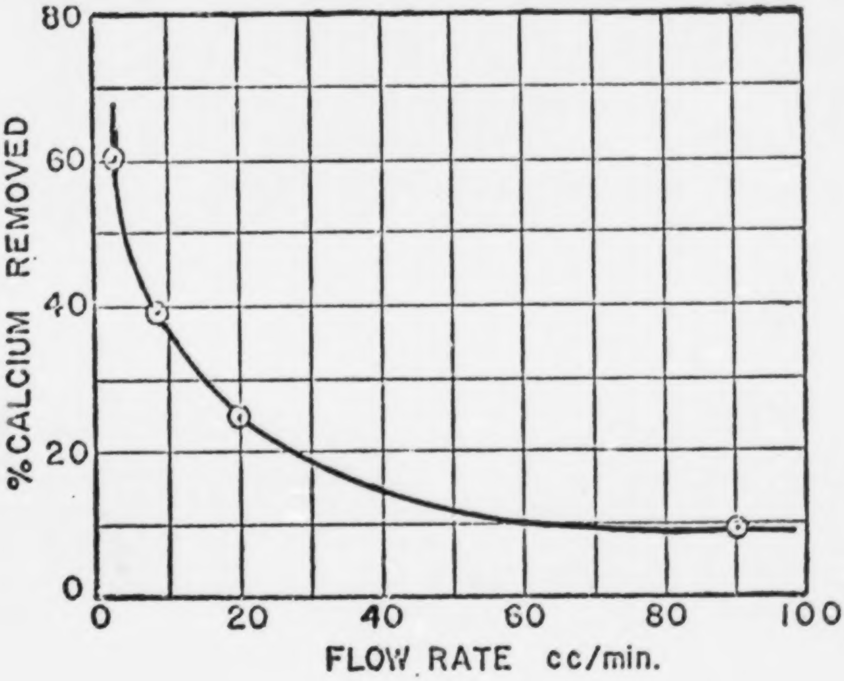

Fig. 35 Removal of Calcium as a Function of Flow Rate.

APPENDIX B

MODELLING EQUILIBRIUM PARTITION COEFFICIENTS OF SOLUTES IN WATER/POLYMER, TWO-PHASE SYSTEMS

by

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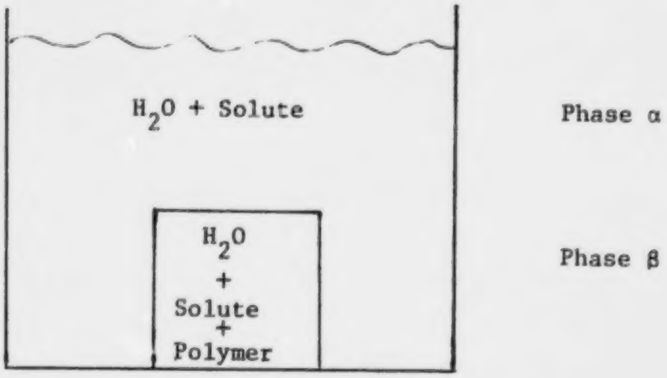
It is well known [see for example Zwolinski et al. (1949), Sourirajan (1970), and Spriggs and Gainer (1973)] that the rejection of a solute by a semi-permeable polymer membrane is strongly influenced by the solubility of that solute in the water/membrane phase. At the request of Gulf South Research Institute, a computational scheme has been devised to model and, once proven, to predict the partition coefficient of the solute in question between the water/polymer phase and the solute/water phase. The analysis is limited to those situations in which the equilibrium solute concentration in the solute/water phase is small, say less than 100 parts per million (ppm) by weight.

In order to fix ideas, consider the system denoted schematically below:



Let us denote as phase "α" the solute/water phase and as phase "β" the solute/polymer/water phase (Let solute = 1, polymer = 2, water = 3). We wish to determine the partition coefficient (PC) of the solute. The partition coefficient at low solute concentrations is given by

$$PC = \phi_1^{\beta}/\phi_1^{\alpha} \tag{20}$$

where ϕ_1^{β} = volume fraction solute in phase β

ϕ_1^{α} = volume fraction solute in phase α

$$\phi_i^{\gamma} = \frac{x_i^{\gamma}\, v_i}{\sum\limits_i x_i^{\gamma}\, v_i}$$

x_i^{γ} = mole fraction in phase γ

v_i = molar volume of i at system temperature and pressure.

We can use conventional polymer solution thermodynamics to obtain the solute PC. At equilibrium, the chemical potentials of solute in phases α and β are equal, or

$$(\mu_1-\mu_1^{\circ})^{\alpha} = (\mu_1-\mu_1^{\circ})^{\beta} \tag{21}$$

where μ_1° = chemical potential of pure, saturated solute at system temperature and pressure

and $(\mu_1^{\circ})^{\alpha} = (\mu_1^{\circ})^{\beta}$

From Flory (1953, p. 549), for a ternary system in which we assume that

(1) No polymer is present in phase $(\phi_2 = 0)$,

(2) The solute concentration in phase α is small, $(\phi_1^{\alpha} << \phi_3^{\alpha})$

(3) The solute concentration in phase β is small $(\phi_1^{\beta} << \phi_2^{\beta})$, and

(4) The molecular weight of the polymer is much larger than that of either the solute or water $(v_1/v_2 = 0$ and $v_3/v_2 = 0)$.

equation (21) becomes

$$PC = \phi_1^{\beta}/\phi_1^{\alpha} = \exp[\phi_2^{\beta}(X_{13}-X_{12}-v_1/v_3)] \tag{22}$$

The parameters X_{13} and X_{12} are binary interaction parameters for interaction between solute and water and between solute and polymer respectively. Equation (22) shows that in order to calculate the solute PC, one must be able to determine X_{13} and X_{12} as well as ϕ_2^{β}, the polymer volume fraction in the swollen, polymer/water phase (β).

Determination of ϕ_2^{β}

We may reasonably assume that the polymer is in swelling equilibrium with water ($\mu_1^{\beta}=\mu_1^{\circ}$), giving [Flory (1953), p. 579],

$$\ln(1-\phi_2^{\beta}) + \phi_2^{\beta} + X_{32}(\phi_2^{\beta}) + \frac{v_3}{v_{2sp}Mc}[(\phi_2^{\beta})^{1/3} - \frac{\phi_2^{\beta}}{2}] = 0 \qquad (23)$$

where X_{32} is a water/polymer interaction parameter, v_{2sp} is polymer specific volume and Mc is the molecular weight of an average segment of polymer molecule between crosslinks.

Equation (23) can be used to obtain ϕ_2^{β} if X_{32} is known, or, alternatively, to obtain X_{32} if ϕ_2^{β} is known.

Determination of Binary Interaction Parameters

A binary interaction parameter for interaction between two substances i and j can be represented by [Hildebrand and Scott, 1964, p. 362]

$$X_{ij} = X_{ij}^{s} + X_{ij}^{h} \qquad (24)$$

where X_{ij}^{s} is a constant, characteristic of the polymer ($X_{ij}^{s} = 0$ if neither i nor j is polymer), and X_{ij}^{h} is proportional to the molar heat of mixing of the solution. Hildebrand and Scott (1964) suggest that X_{ij}^{h} can be calculated for non-polar systems using solubility parameters:

$$X_{ij}^{h} = \frac{v_i(\delta_i-\delta_j)^2}{RT} \qquad (25)$$

where δ_i and δ_j are the solubility parameters of substances i and j, respectively. X_{ij}^{s} must be determined from experimental data [Blanks and Prausnitz (1964)].

Hansen (1967a, b; 1971) has extended the Hildebrand concept to polar and associating systems by defining a "three-dimensional" solubility parameter:

$$\delta = (\delta_d^{2} + \delta_p^{2} + \delta_h^{2})^{1/2} \qquad (26)$$

where δ_d, δ_p, and δ_h are, respectively, the contributions of dispersion forces, dipole interactions, and weak chemical association such as hydrogen bonding. Values of δ_d, δ_p, and δ_h have been tabulated by Hansen (1971) for a variety of non-polymeric substances. Weimer and Prausnitz (1965) have suggested that since polar and associating forces are directional that a more accurate representation of X_{ij}^{h} is given by

$$X_{ij}^{h} = \frac{v_i[(\delta_{di}-\delta_{dj})^2 + (\tau_i-\tau_j)^2 - 2\Psi_{12}]}{RT} \qquad (27)$$

where $\tau_i = (\delta_p^{2} + \delta_h^{2})^{1/2}$

Ψ_{12} = a constant

A similar approach has been suggested by Helpinstill and Van Winkle (1968). Both approaches suffer from a major defect: the parameter Ψ_{12} accounting for the directional nature of the forces cannot be predicted _a priori_.

In this work, we have chosen to use equations (24), (25), and (26) to calculate X_{12}, the solute/polymer interaction parameter.

Unfortunately, we cannot as readily calculate X_{13} and X_{23}, because the values of the components of the solubility parameter of water are highly uncertain [Hansen (1971)]. We resort, therefore, to experimental data to deduce X_{13} and X_{23}. To obtain X_{13}, one may use the fact that at small concentrations of solute in water, Henry's Law holds;

$$p_1 = H_{1,3}\phi_1 \qquad (28)$$

Thus, $H_{1,3} = \lim_{\phi_1 \to 0}(p_1/\phi_1)$ where p_1 is the solute partial pressure above a solute/water solution. Now, for a binary solution at modest pressures, we have [Flory (1953)]

$$\ln(p_1/p_1^s) = \ln\phi_1 + (1-v_1/v_3)\phi + X_{13}\phi_3^2 \qquad (29)$$

where p_1^s is the solute vapor pressure at system temperature. Combining equations (28) and (29), one can solve for X_{13} for a given value of ϕ_1 if $H_{1,3}$ is known from experimental data.

To obtain X_{23}, we use values of ϕ_2^β obtained from swelling measurements.

Test of the Method

Personnel at Gulf South Research Institute have determined values of PC for various solutes in water using cellulose acetate (D.S. = 2). These data are listed in Table

From Thomas and Barker (1963), we calculate $\phi_2^\beta = 0.888$ at 20°C (based on a polymer density of 1.31 g/cm^3). Moore *et al*. (1957) show that for cellulose acetate $X_{12}^s = 0.12$, and $\delta_2 = 11.0(\text{cal/cm}^3)^{1/2}$.

Unfortunately, data of the type required to calculate X_{13} are very scarce. In fact, we have only been able to find such data for *n*-butanol. An exhaustive search of the published literature may, however, reveal more data of this type. Due to the dearth of data with which to calculate X_{13}, we illustrate the PC calculation only for *n*-butanol/cellulose acetate/water.

From Hildebrand and Scott (1964), p. 264, we have for _n_-butanol at 20° C data showing that p_1=1 mm Hg for ϕ_1=0.0232 and p_1^s=4.4 mm Hg. Using equation (29), we find $X_{13} = 6.56^*$. Using the result of Moore _et al._ (1957) for cellulose acetate and δ_1=11.3 $(\mathrm{cal/cm}^3)^{1/2}$ from Hansen (1971), we obtain X_{12}=0.13 at 20°C. Finally, substituting X_{12}, ϕ_2^β, and X_{13} into equation (22), we have PC = 3.3. This result is in order-of-magnitude agreement with the value of 2.5 shown in Table .

Discussion of Results and Conclusion

We have presented a means of computing solute PC's in a solute/water/polymer system based on limited experimental data. The PC calculated for one system is in order-of-magnitude agreement with the corresponding experimental result.

SOLUTE PARTITION COEFFICIENTS (PC) IN WATER/CELLULOSE ACETATE

Solute	PC (20°C)*	Total Solute Originally H_2O, ppm (wt.)**
Bis-(2-chloroethyl) ether	27	40
n-butanol	2.5	40
Methyl ethyl ketone	1.0	150
Dimethyl phthalate	19.	32.5
Glucose	11.8	22.5
Acrylamide	2.5	27
Phenol	38.	48.5
Xylene	56.	12.5
Acetophenone	38.5	100.
Ethylene glycol	5.5	47.

*Total amount of water = 10ml; weight of polymer = 0.29 g; PC = $\phi_1^{\beta}/\phi_1^{\alpha}$.

**PPM quantities represent the molar equivalent amount of potassium hydrogen phthalate in H_2O.

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APPENDIX B

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APPENDIX C

TABLES OF REVERSE OSMOSIS MEMBRANE SEPARATIONS OF ORGANIC SOLUTES FROM WATER

Literature Review of Rejection Coefficients

Prepared by: Donald Mouledoux and Israel Cabasso

November 1974

PREFACE TO THE TABLES

This review contains four types of reverse osmosis membranes: cellulose acetate, cellulose acetate-butyrate, NS-1 (polyurea), and polyamide (including the DuPont nylon hollow fiber membranes). The rejection results were collected from 17 publications and a list of references is given. Many of the rejection values reported in the literature were expressed graphically in figures rather than in tabular form. Thus the rejection data were extrapolated from the figures when precise rejection values could not be found in the cited sources. This may have introduced a deviation or an error of (100 -R%) ± 2% from the true rejection measured by the investigators. The hydraulic permeability L_p is expressed in g/cm^2 sec atm. When the precise value could not be found the L_p was calculated from the reported flux of pure water through the membrane at a given pressure. Calculations were made according to the equation $J_w = L_p \Delta P$. The variations in L_p's for a certain type of membrane result from different membrane casting procedures, different treatments, etc. Some solutes' rejections are sharply influenced by the pH of the water solutions, and pH data are given when available. The cellulose acetate table has a supplemental addition; compounds which are not listed in their class groups may be found in the supplement. Salt rejections(NaCl) of the cellulose acetate membranes reported in Table 1 also are given as a supplement. The reflection coefficients σ (σ = R at infinite pressure) were calculated for several solute-membrane combinations and are given in Tables 5 and 6.

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Table 2 Rejection Data for NS-1 Membranes 168

Table 3 Cellulose Acetate Butyrate 175

Table 4 Rejection Data for Polyamide Membranes 177

INDEX: COMPOUNDS BY CLASSES

Class	Membrane	Appendix C Page No.
Acids		
Monocarboxilic		
	Cellulose Acetate	148-152
	NS-1	171-172
	Cellulose Acetate Butyrate	175
	Polyamide	178
Dicarboxylic		
	Cellulose Acetate	152-153
Alcohols		
Monohydric		
	Cellulose Acetate	139-140
	NS-1	168-169
	Cellulose Acetate Butyrate	175
	Polyamide	177
Polyhydric		
	Cellulose Acetate	143-145
	NS-1	173-174
	Cellulose Acetate Butyrate	176
	Polyamide	178-179
Aldehydes		
	Cellulose Acetate	153-154
	NS-1	170
	Cellulose Acetate Butyrate	175
	Polyamide	178
Amides		
	Cellulose Acetate	165
	NS-1	174

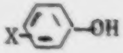
Class	Membrane	Appendix C Page No.
Amides (Cont.)		
	Cellulose Acetate Butyrate	176
	Polyamide	179
Amines		
Primary		
	Cellulose Acetate	160-161
	NS-1	172
	Cellulose Acetate Butyrate	176
	Polyamide	179
Secondary		
	Cellulose Acetate	162
Tertiary		
	Cellulose Acetate	162-163
	NS-1	172
Esters		
	Cellulose Acetate	158-159
	NS-1	173
	Cellulose Acetate Butyrate	176
	Polyamide	179
Ethers		
Cyclic		
	Cellulose Acetate	157-158
Noncyclic		
	Cellulose Acetate	156-157
	NS-1	173
	Cellulose Acetate Butyrate	175
	Polyamide	178

Class	Membrane	Appendix C Page No.
Hydrocarbons		
Aromatic		
	Cellulose Acetate	145-146
Cyclic		
	Cellulose Acetate	147-165
Noncyclic		
	Cellulose Acetate	147-148 165-166
Ketones		
	Cellulose Acetate	154-155
	NS-1	171
	Cellulose Acetate Butyrate	175
	Polyamide	178
Miscellaneous		
	Cellulose Acetate	163-166
Phenols		
	Cellulose Acetate	141-143, 164, 166
	NS-1	169-170
	Cellulose Acetate Butyrate	176
	Polyamide	179
Salts		
NaCl		
	Cellulose Acetate	167
	NS-1	174
	Cellulose Acetate Butyrate	176
	Polyamide	180
Others		
	Cellulose Acetate	164

TABLE 1 REJECTION DATA FOR CELLULOSE ACETATE MEMBRANES

No.	Solute	Formula	M.W.	Conc. ppm	Lp x10^5	Press. atm	Rej. %	Remarks	Ref
	Alcohols	R in ROH							
1.	Ethyl Alcohol	C_2H_5	46.1	100	4.6	17.0	10		1
				1000	0.6	40.8	24		2
				"	1.0	"	13	pH 5.42	2
				"	0.6	102	37	"	2
				"	1.0	"	18		2
2.	n-Propanol	n-C_3H_7	60.1	100	4.6	17.0	24		1
3.	i-Propanol	i-C_3H_7	60.1	"	"	"	37		1
				1000	0.6	40.8	60	pH 5.91	2
				"	1.0	"	44	"	2
				"	0.6	102	77	"	2
				"	1.0	"	52	"	2
4.	Methanol	CH_3	32.0	100	4.6	17.0	5		1
				1000	0.6	40.8	-20	pH 5.77	2
				"	1.0	"	-8	"	2
				"	0.6	102	-12	"	2

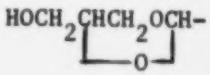
No.	Solute	Formula	M.W.	Conc. ppm	Lp x10^5	Press. atm	Rej. %	Remarks	Ref.
	Alcohols								
4.	Methanol	CH_3	32.0	1000	1.0	102	-8	pH 5.77	2
5.	n-Butyl Alcohol	$n\text{-}C_4H_9$	74.1	100	4.6	17.0	16		1
6.	i-Butyl Alcohol	$i\text{-}C_4H_9$	74.1	"	"	"	41		1
7.	s-Butyl Alcohol	$s\text{-}C_4H_9$	74.1	"	"	"	34		1
8.	t-Butyl Alcohol	$t\text{-}C_4H_9$	74.1	"	"	"	79		1
9.	3-Pentanol	$3\text{-}C_5H_{11}$	88.2	"	"	"	40		1
10.	n-Amyl Alcohol	$n\text{-}C_5H_{11}$	88.2	"	"	"	23		1
11.	n-Hexyl Alcohol	$n\text{-}C_6H_{13}$	102.2	"	"	"	11		1
12	Cyclohexanol	Cyclo C_6H_{11}	100.2	"	"	"	60		1
13.	n-Heptyl Alcohol	$n\text{-}C_7H_{15}$	116.2	"	"	"	9		1
14.	n-Octyl Alcohol	$n\text{-}C_8H_{17}$	130.2	"	"	"	23		1
15.	Benzyl Alcohol	$C_6H_5(CH_2)$	108.1	"	"	"	5		1
16.	Phenethyl Alcohol	$C_6H_5(CH_2)_2$	122.2	"	"	"	8		1

No.	Solute	Formula	M.W.	Conc. ppm	Lp x10^5	Press. atm	Rej. %	Remarks	Ref.
	Phenols	X in 							
17.	Phenol	H	94.1	1000	1.0	102.0	-18	pH 6.25	2
				"	.6	40.8	-6	"	2
				100	4.6	17.0	1		1,4
	Substituted Phenols								
18.	Chlorophenol	Cl	128.6	"	"	"	22		4
19.	m-Chlorophenol	m-Cl	128.6	"	"	"	20		4
20.	p-Chlorophenol	p-Cl	128.6	"	"	"	21		4
21.	Pyrocatechol	o-OH	110.1	"	"	"	2		1
22.	Resorcinol	m-OH	110.1	"	"	"	-1		1
				"	"	"	0		4
23.	Hydroquinone	p-OH	110.1	"	"	"	1		1
				1000	1.0	40.8	-0.63	pH 5.20	2
				"	0.6	40.8	7.03	pH 5.20	2
				"	1.0	102.0	-8.20	"	2
				"	0.6	"	18.19	"	2
				100	4.6	17.0	4.0		4
24.	p-Aminophenol	p-NH_2	109.1	"	"	"	27.0		4

No.	Solute	Formula	M.W.	Conc. ppm.	Lp x10^5	Press. atm	Rej. %	Remarks	Ref.
25.	p-Methoxyphenol	p-OCH_3	124.1	100	4.6	17.0	0		4
26.	p-Cresol	p-CH_3	108.1	"	"	"	2		4
27.	m-Cresol	m-CH_3	108.1	"	"	"	2		4
28.	2,4 Dichlorophenol	o&p Cl	163.0	35	-	120.0	-34		5
29.	m-Nitrophenol	m-NO_2	139.1	100	4.6	17.0	2		4
30.	p-Nitrophenol	p-NO_2	139.1	-	-	20.4	-10	pH 3.0	7
				-	-	"	70	pH 8.5	7
				-	-	27	-13	pH 3.0	7
				-	-	"	78	pH 8.5	7
				-	-	41	-21	pH 3.0	7
				-	-	"	80	pH 8.5	7
				-	-	55	-28	pH 3.0	7
				-	-	"	81	pH 8.5	7
				-	-	68	-37	pH 3.0	7
				-	-	"	82	pH 8.5	7

No.	Solute	Formula	M.W.	Conc. ppm	Lp_5 x10	Press. atm	Rej. %	Remarks	Ref.
	Substituted Phenols (cont.)								
30.	p-Nitrophenol	$p\text{-}NO_2$	139.1	100	4.6	17.0	0		4
	Polyhydric Alcohols								
31.	D-Sorbitol	$CH_2OH(CHOH)_4$- $-CH_2OH$	182.2	"	"	"	99		1
32.	Dulcitol		182.2	"	"	"	99		1
33.	Arabitol	$CH_2OH(CHOH)_3$- $-CH_2OH$	152.2	"	"	"	97		1
34.	Xylitol		152.2	"	"	"	97		1
35.	Adonitol		152.2	"	"	"	97		1
36.	1-Erythritol	$CH_2OH(CHOH)_2$- $-CH_2OH$	122.1	"	"	"	94		1

No.	Solute	Formula	M.W.	Conc. ppm	Lp_5 x10	Press. atm	Rej. %	Remarks	Ref.
41.	Glycerol (cont.)	$CH_2OHCHOH$- -CH_2OH	92.1	1000	0.6	102.0	98	pH 5.95	2
				"	1.0	"	85	"	2
42.	Triethylene Glycol	$HOCH_2CH_2OCH_2$- -$CH_2OCH_2CH_2OH$	150.0	-	-	100	37		12
43.	Propylene Glycol	$CH_2OHCHOH$- -CH_3	76.1	100	4.6	17.0	68		1
44.	*cis*-and-*trans*-1,2-Cyclohexanediol	CHOHCHOH- -$(CH_2)_4$	116.2	"	"	102.0	83		1
45.	*trans*-1,2-Cyclohexanediol		116.2	"	"	"	86		1
46.	1,6 Hexanediol	$CH_2OH(CH_2)_4$- -CH_2OH	118.2	"	"	"	45		1

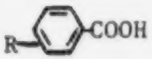
No.	Solute	Formula	M.W.	Conc. ppm	Lp x10^5	Press. atm	Rej. %	Remarks	Ref.
	Polyhydric Alcohols (cont.)								
47.	1,5 Pentanediol	$CH_2OH(CH_2)_3-$ $-CH_2OH$	104.2	100	4.6	102.0	54		1
48.	1,3 Propanediol	CH_2OHCH_2- $-CH_2OH$	76.1	"	"	"	48		1
49.	Dextrose	 $HOCH_2CHCH_2OCH-$ $-CHO$	180.2	940	-	102.0	99.7	pH 7	5
	Aromatics								
50.	Benzene	C_6H_6	78.11	100	4.6	17.0	76		3
				"	"	3.4	97		3
				"	"	6.8	89		3
				"	"	33.8	54		3
51.	Toluene	$C_6H_5CH_3$	92.13	"	"	17.0	73		3

No.	Solute	Formula	M.W.	Conc. ppm	Lp x10^5	Press. atm	Rej. %	Remarks	Ref.
	Aromatics (cont.)								
52.	Cumene	$C_6H_5CH(CH_3)_2$	120.19	100	4.6	17.0	80		3
				"	"	6.8	98		3
				"	"	33.8	71		3
				"	"	67.6	53		3
				"	"	102.0	35		3
53.	Styrene	$C_6H_5CH=CH_2$	104.14	"	"	17.0	70		3
54.	Ethylbenzene	$C_6H_5CH_2CH_5$	106.16	"	"	"	78		3
55.	o-Xylene	$C_6H_4(CH_3)_2$	106.16	"	"	"	86		3
56.	m-Xylene			"	"	"	84		3
57.	p-Xylene			"	"	"	85		3
58.	Propylbenzene	$C_6H_5C_3H_7$	120.19	"	"	"	98		3
59.	t-Butylbenzene	$C_6H_5C(CH_3)_3$	134.12	"	"	"	99		3

No.	Solute	Formula	M.W.	Conc. ppm	Lp_5 x10	Press. atm	Rej. %	Remarks	Ref.
	Cyclic Hydrocarbons								
60.	Cyclopentene	$\underline{-CH=CH(CH_2)_3-}$	68.11	100	4.6	17.0	60		3
61.	Cyclohexane	$\underline{-(CH_2)_6-}$	84.16	"	"	"	90		3
	Hydrocarbons								
62.	1,6 Heptadiyne	$CH\equiv C(CH_2)_3-$ $-C\equiv CH$	92.13	"	"	"	42		3
63.	Isoprene	$CH_2=C(CH_3)-$ $-CH=CH_2$	68.11	"	"	"	52		3
64.	1-Hexyne	$CH\equiv C(CH_2)_3-$ $-CH_3$	82.14	"	"	"	54		3
65.	1,5 Hexadiene	$CH_2=CH(CH_2)_2-$ $-CH=CH_2$	82.14	"	"	"	59		3

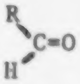
No.	Solute	Formula	M.W.	Conc. ppm	Lp $\times 10^5$	Press. atm	Rej. %	Remarks	Ref.
	Hydrocarbons								
66.	1-Heptyne	$CH\equiv C(CH_2)_3$- -CH_3	96.17	100	4.6	17.0	77		3
67.	4-Methyl-1-pentene	CH_2=$CHCH_2$- -$CH(CH_3)CH_3$	84.16	"	"	"	90		3
68.	1-Hexene	CH_2=$CH(CH_2)_3$- -CH_3	84.16	"	"	"	90		3
69.	n-Hexane	$CH_3(CH_2)_4$- -CH_3	86.17	"	"	"	99		3
	Monocarboxilic Acids								
	Acid	R in R-COOH							
70.	Pivalic acid	t-C_4H_9	102.1	"	"	"	66		4
71.	i-Butyric acid	i-C_3H_7	88.1	"	"	"	35		4

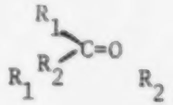
No.	Solute	Formula	M.W.	Conc. ppm	L_p x10^5	Press. atm	Rej. %	Remarks	Ref.
	Monocarboxilic Acids (cont.)								
72.	Valeric acid	n-C_4H_9	102.1	100	4.6	17.0	19		4
73.	n-Butyric acid	n-C_3H_7	88.1	"	"	"	25		4
74.	Propionic acid	n-C_2H_5	74.1	"	"	"	24		4
75.	Acetic acid	CH_3	60.1	"	"	"	24		4
				1000	1.0	40.8	10	pH 3.97	2
				"	0.6	"	18	"	2
				"	1.0	102.0	18	"	2
				"	0.6	"	30	"	2
76.	4-Phenylbutyric acid	$C_6H_5(CH_2)_3$	164.2	100	4.6	"	22		4
77.	3-Phenylpropionic acid	$C_6H_5(CH_2)_2$	150.2	"	"	"	18		4

No.	Solute	Formula	M.W.	Conc. ppm	Lp x10^5	Press. atm	Rej. %	Remarks	Ref.
	Monocarboxilic Acids (cont.)								
78.	Phenylacetic acid	$C_6H_5CH_2$	136.1	100	4.6	102.0	26		4
				"	"	34.0	29		7
79.	Benzoic acid	C_6H_5	122.1	"	"	17.0	19		4
80.	Caprylic acid	$n-C_7H_{15}$	144.2	"	"	"	19		4
81.	L-Leucine	$(CH_3)_2CHCH_2-$ $-CH(NH_2)$	131.2	1312	-	40	96	pH 3.6	13
				"	-	"	98	pH 4.5	13
	R in			"	-	"	99	pH 5.8	13
82.	p-Aminobenzoic acid	$p-NH_2$	137.1	137	4.6	17.0	13		4
				"	-	40	2	pH 4.2	13
				"	-	"	12	pH 3.2	13
				"	-	"	59	pH 2.3	13
				"	-	"	75	pH 1.7	13

No.	Solute	Formula	M.W.	Conc. ppm	Lp x10^5	Press. atm	Rej. %	Remarks	Ref.
	Monocarboxilic Acids (cont.)								
83.	m-Aminobenzoic acid	m-NH_2	137.1	137	-	40	57	pH 3.9	13
				"	-	"	70	pH 3.1	13
				"	-	"	88	pH 2.4	13
				"	-	"	90	pH 2.0	13
				"	-	"	96	pH 1.8	13
84.	Anicic acid	p-OCH_3	152.1	100	4.6	17.0	20		4
85.	m-Toluic	m-CH_3	136.1	"	"	"	23		4
86.	m-Hydroxybenzoic acid	m-OH	138.1	"	"	"	19		4
87.	m-Nitrobenzoic acid	m-NO_2	167.1	"	"	"	37		4
88.	o-Nitrobenzoic acid	o-NO_2	167.1	"	"	"	76		4

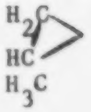
No.	Solute	Formula	M.W.	Conc. ppm	Lp_5 x10^5	Press. atm	Rej. %	Remarks	Ref.
	Monocarboxilic Acids (cont.)								
89.	p-Nitrobenzoic	p-NO_2	167.1	100	4.6	17.0	35		4
90.	o-Chlorobenzoic	o-Cl	156.6	"	"	"	45		4
	Dicarboxylic Acids								
	Acid	R inR$(COOH)_2$							
91.	Oxalic acid	—	90.0	"	"	"	94		6
92.	Malonic	$-CH_2-$	104.1	"	"	"	55		6
93.	Succinic acid	$-(CH_2)_2-$	118.1	"	"	"	50		6
94.	Adipic	$-(CH_2)_4-$	146.1	"	"	"	41		6
95.	Pimelic acid	$-(CH_2)_5-$	160.2	"	"	"	36		6
96.	Suberic	$-(CH_2)_6-$	174.2	"	"	"	25		6

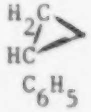
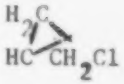
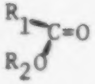
No.	Solute	Formula	M.W.	Conc. ppm	Lp_5 x10	Press. atm	Rej. %	Remarks	Ref.
	Dicarboxylic Acids (cont.)								
97.	Azelaic	$(CH_2)_7$	188.2	100	4.6	17.0	15		6
	Aldehydes	R in 							
98.	Formaldehyde	H	30.0	1000	0.6	40.8	33	pH 4.64	2
				"	1.0	"	20	"	2
				"	0.6	102.0	48	"	2
				"	1.0	"	30	"	2
99.	Acetaldehyde	CH_3	44.1	"	4.6	17.0	60		8
100.	Propionaldehyde	C_2H_5	58.1	"	"	"	75		8
101.	n-Butylaldehyde	$n\text{-}C_3H_7$	72.1	"	"	"	60		8
102.	i-Butyl aldehyde	$i\text{-}C_3H_7$	72.1	100	"	"	78		8
103.	Crotonaldehyde	$CH_3CH{=}CH$	70.1	"	"	"	15		8

No.	Solute	Formula	M.W.	Conc. ppm	Lp $x10^5$	Press. atm	Rej. %	Remarks	Ref.
	Aldehydes (cont.)								
104.	Furfuryl	C_4H_3O	96.1	100	4.6	17.0	2		8
105.	Benzaldehyde	C_6H_5	106.1	"	"	"	10		8
	Ketones								
106.	Acetone	CH_3, CH_3	58.1	"	"	"	22		8
				"	-	102.0	17		7
					-	100	47		9
				1000	1.0	40.8	5	pH 5.48	2
				"	0.6	40.8	23	"	2
				"	1.0	102.0	6	"	2
				"	0.6	102.0	30	"	2
107.	Methyl Ethyl Ketone	CH_3, C_2H_5	72.1	100	4.6	17.0	24		8

No.	Solute	Formula	M.W.	Conc. ppm	Lp $x10^5$	Press. atm	Rej. %	Remarks	Ref.
107.	Methyl Ethyl Ketone (cont.)	CH_3, C_2H_5	72.1	-	-	163	18		10
108.	Cyclopentanone	cyclo-C_4H_8	84.1	100	4.6	17.0	26		8
109.	Cyclohexanone	cyclo-C_5H_{10}	98.1	"	"	"	39		8
110.	Diisopropyl Ketone	iC_3H_7, iC_3H_7	114.2	"	"	"	67		8
111.	Diisobutyl Ketone	iC_4H_9, iC_4H_9	142.2	"	"	"	59		8
112.	Benzyl Methyl Ketone	$C_6H_5(CH_2)$, CH_3	134.2	"	"	"	17		8
113.	Acetophenone	C_6H_5, CH_3	120.1	"	"	"	17		8

No.	Solute	Formula	M.W.	Conc. ppm	Lp $x10^5$	Press. atm	Rej. %	Remarks	Ref.
	Ethers - Noncyclic	R_1-O-R_2							
114.	Diethyl ether	C_2H_5, C_2H_5	74.1	100	4.6	17.0	57		8
				1000	1.0	40.8	12.5	pH 5.59	2
				"	0.6	"	30.2	"	2
				"	1.0	102.0	10	"	2
				"	0.6	"	24	"	2
115.	Diisopropyl ether	iC_3H_7, iC_3H_7	102.2	100	4.6	17.0	84		8
116.	Anisole	CH_3, C_6H_5	108.1	"	"	"	51		8
117.	Ethyl vinyl ether	C_2H_5, $H_2C{=}CH$	72.1	"	"	"	55		8
118.	Phenetole	C_2H_5, C_6H_5	122.2	"	"	"	46		8
119.	Methyl benzyl ether	CH_3, $C_6H_5(CH_2)$	122.2	"	"	"	26		8

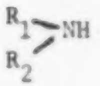
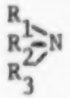
No.	Solute	Formula	M.W.	Conc. ppm	Lp $x10^5$	Press. atm	Rej. %	Remarks	Ref.
	Ethers (cont.)								
120.	Polyoxyethylene Nonylphenyl ether	C_9H_{19}- -$(CH_2CH_2O)nH$-							
	(NP-10)	n=10	661.41	52	3.07	40	83.9		14
	(NP-16)	n=16	925.5	100	2.75		59.5		14
	(NP-27)	n-27	1409.6	238	2.88		92		14
	Cyclic Ethers	cyclo >O							
121.	Tetrahydropyran	cyclo- $-C_5H_{10}$	86.1	100	4.6	17.0	47		8
122.	Tetrahydrofuran	cyclo- $-C_4H_8$	72.1	"	"	"	53		8
123.	1,4 Dioxane	C_4H_6O	88.1	"	"	"	49		8
124.	Propylene Oxide		58.1	"	"	"	33		8

No.	Solute	Formula	M.W.	Conc. ppm	Lp x10^5	Press. atm	Rej. %	Remarks	Ref.
	Cyclic Ethers (cont.)								
125.	Styrene oxide		120.1	100	4.6	17.0	26		8
126.	Epichlorohydrin		92.5	"	"	"	18		8
	Esters	R_1, R_2 in 							
127.	n-Amyl Acetate	CH_3, n-C_5H_9	130.2	"	"	"	50		8
128.	Methyl n-Butyrate	C_3H_7, CH_3	102.1	"	"	"	44		8
129.	Ethyl acetate	CH_3, C_2H_5	88.1	"	"	"	45		8
130.	Methyl acetate	CH_3, CH_3	74.1	"	"	"	40		8
				1000	1.0	40.8	-3.53	pH 5.34	2
				"	0.6	"	20.7	"	2

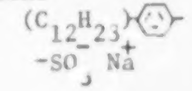
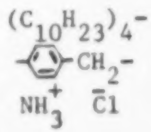
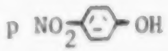
No.	Solute	Formula	M.W.	Conc. ppm	Lp x10^5	Press. atm	Rej. %	Remarks	Ref.
130.	Methyl acetate (cont.)	CH_3, CH_3	74.1	1000	1.0	102.0	11.14	pH 5.38	2
				"	0.6	"	12.36	"	2
131.	Methyl benzoate	C_6H_5, CH_3	136.1	100	4.6	17.0	25		8
132.	Ethyl chloroacetate	$ClCH_2$, C_2H_5	122.6	"	"	"	9		8
133.	Methyl chloroacetate	$ClCH_2$, CH_3	108.5	"	"	"	13		8
134.	Vinyl acetate	CH_3, $H_2C{=}CH$	86.1	"	"	"	3		8
135.	Methyl acrylate	$H_2C{=}CH$, CH_3	86.1	"	"	"	35		8
136.	Methyl methacrylate	$H_2C{=}CCH_3$, CH_3	100.1	"	"	"	40		8

No.	Solute	Formula	M.W.	Conc. ppm	Lp x10^5	Press. atm	Rej. %	Remarks	Ref.
	Primary Amines								
	Amine	R in RNH_2							
137.	Aniline	C_6H_5	93.1	100	4.6	17.0	4		8
				1000	1.0	40.8	-9	pH 6.62	2
				"	0.6	"	22	"	2
				"	1.0	102.0	-5	"	2
				"	0.6	"	17	"	2
				-	-	34	88	pH 6.4	7
				-	-	"	9	pH 7.3	7
				-	-	68	78	pH 6.4	7
				-	-	"	4	pH 7.5	7
138.	p-Anisidine	p-$CH_3OC_6H_4$	123.2	100	4.6	17.0	4		8
139.	o-Anisidine	o-$CH_3OC_6H_4$	123.2	"	"	"	8		8

No.	Solute	Formula	M.W.	Conc. ppm	Lp x10^5	Press. atm	Rej. %	Remarks	Ref.
	Primary Amines (cont.)								
140.	p-Toluidine	p-$CH_3C_6H_4$	107.2	100	4.6	17.0	7		8
141.	m-Toluidine	m-$CH_3C_6H_4$	107.2	"	"	"	7		8
142.	o-Toluidine	o-$CH_3C_6H_4$	107.2	"	"	"	7		8
143.	m-Phenylenediamine	m-$NH_2C_6H_4$	108.2	"	"	"	15		8
144.	o-Phenylenediamine	o-$NH_2C_6H_4$	108.2	"	"	"	14		8
145.	p-Chloroaniline	p-ClC_6H_4	127.6	"	"	"	14		8
146.	o-Chloroaniline	o-ClC_6H_4	127.6	"	"	"	19		8
147.	m-Chloroaniline	m-ClC_6H_4	127.6	"	"	"	21		8
148.	m-Nitroaniline	m-$NO_2C_6H_4$	138.1	"	"	"	8		8

No.	Solute	Formula	M.W.	Conc. ppm	Lp_5 x10^5	Press. atm	Rej. %	Remarks	Ref.
	Secondary Amines	R_1, R_2 in  R_1R_2NH							
149.	Di-n-Butylamine	$n-C_4H_9$, $n-C_4H_9$	129.5	100	4.6	17.0	63		8
150.	Piperidine	cyclo-C_5H_{10}	85.2	"	"	"	88		8
151.	Dimethylamine	CH_3, CH_3	45.1	"	"	"	16		8
152.	Diisopropylamine	$i-C_3H_7$, iC_3H_7	101	-	-	-	72		12
153.	N-Methylaniline	C_6H_5, CH_3	107.2	100	4.6	17.0	12		8
	Tertiary Amines	R_1, R_2, R_3 in  $R_1R_2R_3N$							
154.	Triethyl	C_2H_5, C_2H_5, C_2H	101.2	"	"	"	95		8

No.	Solute	Formula	M.W.	Conc. ppm	Lp x10^5	Press. atm	Rej. %	Remarks	Ref.
	Tertiary Amines (cont.)								
155.	Trimethyl	CH_3, CH_3, CH_3	59.1	100	4.6	17.0	77		8
156.	N,N-Dimethyl-benzylamine	CH_3, CH_3, $C_6H_5(CH_2)$	135.2	"	"	"	56		8
157.	N,N-Dimethyl-aniline	CH_3, CH_3, C_6H_5	121.2	"	"	"	33		8
	Supplementary								
158.	Nitromethane	CH_3NO_2	61.0	-	-	34	-6	pH 7.2	7
				-	-	68	-9	"	7
159.	Boric Acid	HBO_2	43.8	-	-	34	43	pH 7.0	7
				-	-	68	67	"	7
				-	-	34	97	pH 11.0	7
				-	-	68	97	"	7

No.	Solute	Formula	M.W.	Conc. ppm	Lp x10^5	Press. atm	Rej. %	Remarks	Ref.
	Supplementary								
160.	Sodium Oleate	$CH_3(CH_2)_7CH{=}CH{-}(CH_2)_7COO^- \overset{+}{Na}$	304.5	-	-	100	99.9	Basic	11
161.	Sodium dodecylbenzene-sulfonate		349.5	210	1.07	40	99.8		14
162.	Tetradecylbenzyl-ammonium chloride		704.6	188	4.03	"	93.7		14
163.	p-Nitrophenol		139.4	-	-	0	0	pH 3.0	7
				-	-	20	-10	"	7
				-	-	27	-14	"	7
				-	-	40.8	-20	"	7
				-	-	54	-27	"	7
				-	-	68	-34	"	7

No.	Solute	Formula	M.W.	Conc. ppm	Lp_5 x10	Press. atm	Rej. %	Remarks	Ref.
	Supplementary (cont.)								
164.	Urea	NH_2CONH_2	60	-	-	100	45		12
				1000	1.0	40	17.56	pH 7.72	2
				"	0.6	"	38.02	"	2
				"	1.0	102.0	26.76	"	2
165.	2,4 Dichlorophenoxy-				0.6	"	24.37		2
	acetic acid	$C_8H_7O_3Cl_2$	221	35	-	102.0	92.8	Herbicide	5
166.	Cycloheptatriene	$CH=CHCH=CH-$ $-CH=CHCH_2$	92.1	100	4.6	17.0	66		3
167.	Cyclohexene	$-CH=CH-$ $(CH_2)_4$	82.1	"	"	"	65		3
168.	Cyclopentane	$(CH_2)_5$	70.1	"	"	"	70		3
169.	Methyl Cyclopentane	$CH(CH_3)(CH_2)_4$	84.2	"	"	"	93		3
170.	1,6-Heptadiene	$CH_2=CH_2(CH_2)_3-$ $-CH=CH$	96.2	"	"	"	94		3

No.	Solute	Formula	M.W.	Conc. ppm	Lp_5 x10	Press. atm	Rej. %	Remarks	Ref.
171	Isopentane	$(CH_3)_2CHCH_2CH_3$	72.2	100	4.6	17.0	87		3
172.	2-Methyl-1-pentene	$CH_2=CHCH_2CH-$ $-(CH_3)_2$	84.2	"	"	"	92		3
20.	p-Chlorophenol	p-Cl		128	4.6	17.0	42		16
				"	"	40.8	20		16
				"	"	68.0	18		16
				"	"	102.0	1		16

Cellulose Acetate's NaCl Rejection

No.	Conc. ppm.	Lp x10^5	Press. atm	Rej. %	Ref.
1	1500	4.6	34.0	94.8	1
2	5000	0.6	17.0	98.5	2
	5000	1.0	17.0	95.7	2
	5000	0.6	40.8	99.1	2
	5000	1.0	40.8	97.3	2
3	--	0.9	68.0	97	7
4	--	0.9	102	98.5	5
5	--	--	12.2	90-95	12
6	5584	--	40	92	13

TABLE 2 REJECTION DATA FOR NS-1 MEMBRANES

No.	Solute	Membrane Designation	Conc. ppm	Lp x10^5	Press. atm	Rej. %	pH	Ref.
1.	Methanol	Standard	1000	1.0	54.4	33.2	-	15
		Modified	"	0.5	"	41.0	-	15
		52C	"	1.1	40.8	-5.98	5.77	2
		53J	"	1.3	"	18.06	"	2
		52C	"	1.1	102	1.41	"	2
		53J	"	1.3	102	9.87	"	2
2.	Ethanol	Standard	"	1.0	54.4	79.8	-	15
		Modified	"	0.5	"	86.7	-	15
		52C	"	1.1	40.8	64.78	5.42	2
		53J	"	1.3	"	65.66	"	2
		52C	"	1.1	102	70.01	"	2
		53J	"	1.3	"	73.57	"	2
3.	n-Propanol	Standard	"	1.0	54.4	92.7	-	15
		Modified	"	0.5	"	93.6	-	15

No.	Solute	Membrane Designation	Conc. ppm	Lp x10^5	Press. atm	Rej. %	pH	Ref.
4.	Isopropanol	Standard	1000	1.0	54.4	91.4	-	15
		Modified	"	0.5	"	92.3	-	15
		52C	"	1.1	40.8	82.01	5.91	2
		53J	"	1.3	"	85.10	"	2
		52C	"	1.1	102.0	56.06	"	2
		53J	"	1.3	"	40.16	"	2
5.	n-Butanol	Standard	"	1.0	54.4	94.2	-	15
		Modified	"	0.5	"	96.3	-	15
6.	n-Pentanol	Standard	"	1.0	54.4	95.2	-	15
		Modified	"	0.5	"	97.7	-	15
7.	3-Pentanol	Standard	"	1.0	54.4	97.9	-	15
		Modified	"	0.5	"	99.4	-	15
8.	Phenol	52C	"	1.1	40.8	68.57	6.25	2
		53J	"	1.3	"	55.68	"	2
		Standard	"	1.0	54.4	84.1	-	15
		Modified	"	0.5	"	87.1	-	15
		52C	"	1.1	102.0	70.21	6.25	2

No.	Solute	Membrane Designation	Conc. ppm	Lp x10^5	Press. atm	Rej. %	pH	Ref.
8.	Phenol (cont.)	53J	1000	1.3	102.0	65.72	6.25	2
9.	p-Chlorophenol	Standard	"	1.0	54.4	81.0	-	15
			"	"	17.0	66	-	15
			"	"	40.8	79	-	15
			"	"	68.0	80	-	15
			"	"	102.0	80	-	15
		Modified	"	0.5	54.4	83.2	-	15
10.	Formaldehyde	52C	"	1.1	40.8	37.05	4.64	2
		53J	"	1.3	"	38.62	"	2
		Standard	"	1.0	54.4	54.7	-	15
		Modified	"	0.5	"	70.0	-	15
		52C	"	1.1	102.0	49.96	4.64	2
		53J	"	1.3	"	50.65	"	2
11.	Acetaldehyde	Standard	"	1.0	54.0	75.0		15
		Modified	"	0.5	"	80.6		15
12.	Benzaldehyde	Standard	"	1.0	"	87.6		15
		Modified	"	0.5	"	95.0		15

No.	Solute	Membrane Designation	Conc. ppm	Lp x10^5	Press. atm	Rej. %	pH	Ref.
13.	Acetone	52C	1000	1.1	40.8	80.44	5.48	2
		53J	"	1.3	"	76.03	"	2
		Standard	"	1.0	54.0	93.4		15
		Modified	"	0.5	"	96.1		15
		52C	"	1.1	102.0	78.26	5.48	2
		53J	"	1.3	"	77.32	"	2
14.	Acetophenone	Standard	500	1.0	54.0	96.7		15
		Modified	"	0.5	"	98.2		15
15.	Cyclohexanone	Standard	"	1.0	"	97.3		15
		Modified	"	0.5	"	98.7		15
16.	Methyl ethyl ketone	Standard	1000	1.0	"	90.8		15
		Modified	"	0.5	"	95.5		15
17.	Acetic acid	52C	"	1.1	40.8	68.70	3.77	2
		53J	"	1.3	"	48.02	"	2
		Standard	"	1.0	54.0	71.0		15
		Modified	"	0.5	"	80.3		15

No.	Solute	Membrane Designation	Conc. ppm	Lp x10^5	Press. atm	Rej. %	pH	Ref.
17.	Acetic acid (cont.)	52C	1000	1.1	102.0	9.00	3.77	2
		53J	"	1.3	"	69.86	"	2
18.	Lactic acid	Standard	"	1.0	54.0	87.6		15
		Modified	"	0.5	"	89.3		15
19.	Benzoic acid	Standard	500	1.0	"	66.3		15
		Modified	"	0.5	"	82.0		15
20.	Ethylamine	Standard	1000	1.0	"	86.2		15
		Modified	"	0.5	"	92.8		15
21.	Triethylamine	Standard	"	1.0	"	99.7		15
		Modified	"	0.5	"	98.5		15
22.	Aniline	52C	"	1.1	40.8	31.36	6.62	2
		53J	"	1.3	"	51.80	"	2
		Standard	"	1.0	54.0	91.8		15
		Modified	"	0.5	"	95.9		15
		52C	"	1.1	102.0	14.99	6.62	2
		53J	"	1.3	"	31.31	"	2

No.	Solute	Membrane Designation	Conc. ppm	Lp_5 $x10^5$	Press. atm	Rej. %	pH	Ref.
23.	Methyl acetate	52C	1000	1.1	40.8	36.37	5.38	2
		53J	"	1.3	"	28.32	"	2
		Standard	"	1.0	54.0	89.2		15
		Modified	"	0.5	"	91.7		15
		52C	"	1.1	102.0	23.02	5.38	2
		53J	"	1.3	"	44.62	"	2
24.	Ethyl acetate	Standard	"	1.0	54.0	95.8		15
		Modified	"	0.5	"	96.9		15
25.	Ethyl ether	52C	"	1.1	40.8	90.93	5.59	2
		53J	"	1.3	"	82.18	"	2
		52C	"	1.1	102.0	65.62	"	2
		53J	"	1.3	"	77.09	"	2
26.	Glycerol	52C	"	1.1	40.8	96.87	5.97	2
		53J	"	1.3	"	89.15	"	2
		52C	"	1.1	102.0	96.18	"	2
		53J	"	1.3	"	91.69	"	2
27.	Hydroquinone	52C	"	1.1	40.8	82.23	5.20	2

No.	Solute	Membrane Designation	Conc. ppm	Lp x10^5	Press. atm	Rej. %	pH	Ref.
27.	Hydroquinone (cont.)	53J	1000	1.3	40.8	71.93	5.20	2
		52C	"	1.1	102.0	86.29	"	2
		53J	"	1.3	"	77.98	"	2
28.	Urea	52C	"	1.1	40.8	64.15	7.72	2
		53J	"	1.3	"	55.37	"	2
		52C	"	1.1	102.0	74.32	"	2
		53J	"	1.3	"	63.38	"	2
29.	NaCl	53J	5000	1.3	40.8	99.71		2
		52C	"	1.1	102.0	99.26		2
		53J	"	1.3	"	99.24		2

TABLE 3 CELLULOSE ACETATE BUTYRATE

No.	Solute	Conc. ppm	Lp x10^5	Press. atm	Rej. %	pH	Ref.
1.	Methanol	1000	0.2	40.8	-9.09	5.77	2
		"	"	102.4	1.27	"	2
2.	Ethanol	"	"	40.8	1.9	5.42	2
		"	"	102.4	14.43	"	2
3.	i-Propanol	"	"	40.8	41.04	5.91	2
		"	"	102.4	57.58	"	2
4.	Acetic Acid	"	"	40.8	12.38	3.77	2
		"	"	102.4	26.18	"	2
5.	Formaldehyde	"	"	40.8	41.05	4.64	2
		"	"	102.4	50.64	"	2
6.	Acetone	"	"	40.8	16.60	5.48	2
		"	"	102.4	6.16	"	2
7.	Ethyl Ether	"	"	40.8	39.51	5.59	2
		"	"	102.4	2.01	"	2

No.	Solute	Conc. ppm	$Lp \times 10^5$	Press atm	Rej. %	pH	Ref.
8.	Glycerol	1000	0.2	40.8	90.21	5.97	2
		"	"	102.4	96.08	"	2
9.	Hydroquinone	"	"	40.8	30.97	5.20	2
		"	"	102.4	38.15	"	2
10.	Phenol	"	"	40.8	10.56	6.25	2
		"	"	102.4	-12.07	"	2
11.	Urea	"	"	40.8	8.00	7.72	2
		"	"	102.4	31.36	"	2
12.	Aniline	"	"	40.8	25.51	6.62	2
		"	"	102.4	-5.19	"	2
13.	Methyl Acetate	"	"	40.8	-25.14	5.38	2
		"	"	102.4	-10.78	"	2
14.	Sodium Chloride	5000	"	40.8	99.6	6.64	2
		"	"	102.4	99.8	"	2

TABLE 4 REJECTION DATA FOR POLYAMIDE MEMBRANES

No.	Solute	Type	Conc. ppm	L_p $\times 10^5$	Press. atm	Rej. %	Remarks	Ref.
1.	Methanol	B-9	536	-	27.2	28.01		2
		B-9	500-2000	-	-	0		17
		-	1000	.43	40.8	19.10	pH 5.77	2
		-	"	"	102.0	5.42	"	2
2.	Ethanol	B-9	677	-	27.2	36.49		2
		B-9	500-2000	-	-	28		17
		-	1000	.43	40.8	57.46	pH 5.42	2
		-	1000	"	102.0	70.45	"	2
3.	1-Propanol	B-9	1174	-	27.2	90.05		2
		B-9	500-2000	-	-	75		17
		-	1000	.43	40.8	88.97	pH 5.91	2
		-	"	"	102.0	95.53	"	2

No.	Solute	Type	Conc. ppm	Lp $\times 10^5$	Press. atm	Rej. %	Remarks	Ref.
4.	Acetic acid	B-9	682	-	27.2	31.28		2
		B-9	500	-	-	40		17
		-	1000	.43	40.8	70.14	pH 3.77	2
		-	"	"	102.0	82.21	"	2
5.	Formaldehyde	B-9	1278	-	27.2	21.19		2
		-	1000	.43	40.8	52.10	pH 4.64	2
		-	"	"	102.0	68.61	"	2
6.	Acetone	B-9	856	-	27.2	52.93		2
		-	1000	.43	40.8	71.96	pH 5.48	2
		-	"	.43	102.0	72.24	"	2
7.	Ethyl ether	B-9	388	-	27.2	57.67		2
		-	1000	.43	40.8	89.74	pH 5.59	2
		-	"	"	102.0	91.67	"	2
8.	Glycerol	B-9	765	-	27.2	87.85		2
		B-9	500-2000	-	-	90		17
		-	1000	.43	40.8	88.04	pH 5.97	2
		-	"	"	102.0	88.14	"	2

No.	Solute	Type	Conc. ppm	L_p x10^5	Press. atm	Rej. %	Remarks	Ref.
9.	Hydroquinone	B-9	551	-	27.2	60.49		2
		-	1000	.43	40.8	84.49	pH 5.20	2
		-	"	"	102.0	98.61	"	2
10.	Phenol	B-9	773	-	27.2	44.67		2
		B-9	500-2000	-	-	55		17
		-	1000	.43	40.8	80.06	pH 6.25	2
		-	"	"	102.0	88.72	"	2
11.	Urea	B-9	1188	-	27.2	34.45		2
		-	1000	.43	40.8	55.41	pH 7.72	2
		-	"	"	102.0	89.32	"	2
12.	Aniline	B-9	440	-	27.2	47.28		2
		-	1000	.43	40.8	78.08	pH 6.62	2
		-	"	"	102.0	82.19	"	2
13.	Methyl Acetate	B-9	370	-	27.2	57.45		2
		-	1000	.43	40.8	54.31	pH 5.38	2
		-	"	"	102.0	44.50	"	2

No.	Solute	Type	Conc. ppm	Lp x10^5	Press. atm	Rej. %	Remarks	Ref.
14.	Sodium chloride	B-9	3850	-	27.2	93.06		2
		B-9	1500	-	-	90		17
		-	5000	.43	40.8	99.13	pH 6.64	2
		-	"	"	102.0	99.58	"	2

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